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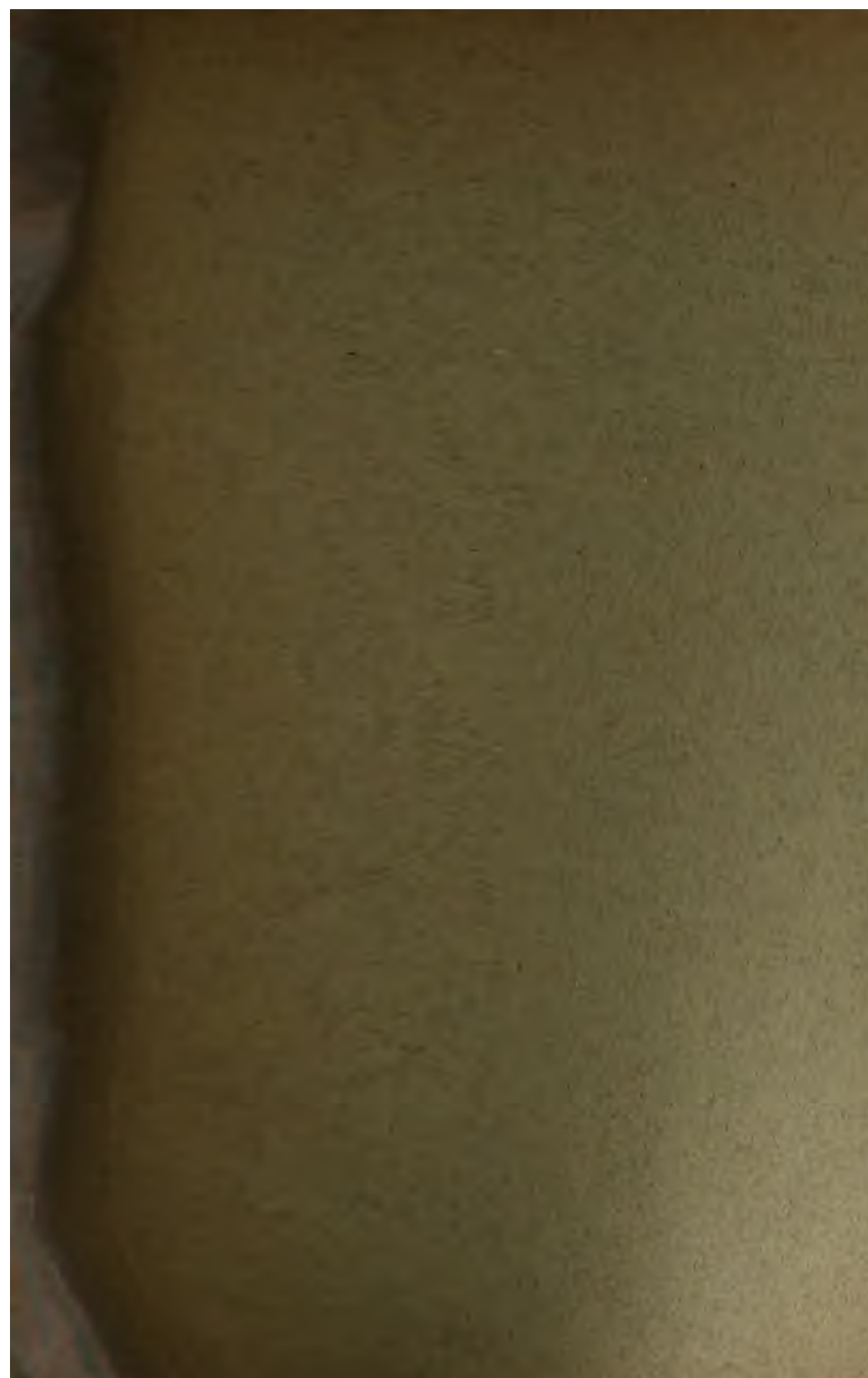


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VOL. XVII.



No. 1.

# THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

## ON THE BEHAVIOR OF ALLYLMALONIC, ALLYLACETIC, AND ETHYLIDENEPROPIONIC ACIDS WHEN BOILED WITH CAUSTIC SODA SOLUTIONS.

CONTRIBUTIONS TO THE KNOWLEDGE OF PROPYLIDENEACETIC  
ACID.<sup>1</sup>

BY JOHN G. SPENZER.

Received October 26, 1894.

**D**URING the preparation of hydropiperic acid, Fittig and Buri,<sup>2</sup> in 1883, discovered that in the reduction of piperic acid by means of sodium amalgam, two very different isomeric hydropiperic acids were formed, according as the reducing fluid was kept almost neutral, or allowed to become strongly alkaline by not adding acid. In the first procedure they obtained the already known and now designated  $\alpha$  hydropiperic acid, while in the second process together with the  $\alpha$  acid, larger or smaller quantities of the new isomeric  $\beta$  hydropiperic acid appeared, which seemed to have been produced from the  $\alpha$  acid through the agency of the caustic soda formed in the reducing fluid.

In fact it was proven experimentally, by heating the  $\alpha$  hydropiperic acid, with caustic soda on the water-bath, that  $\beta$  hydropiperic acid could be obtained.

Weinstein<sup>3</sup> and Regel<sup>4</sup> were induced by Fittig to examine the two isomeric acids further, and because of its behavior on substituting bromine and hydrobromic acid as also in the oxidation with potassium permanganate they came to the interesting con-

<sup>1</sup> Read before Section C., American Association for Advancement of Science, Brooklyn, N. Y., August 20, 1894.

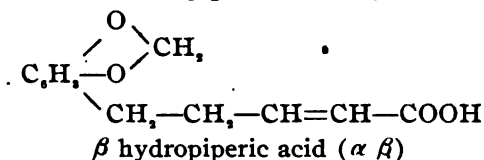
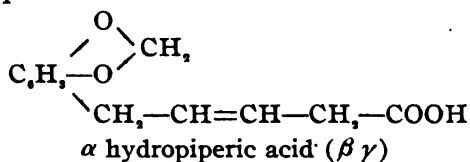
<sup>2</sup> *Ann. Chem.*, 216, 171.

<sup>3</sup> *Ibid.*, 227, 31.

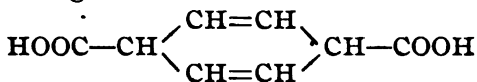
<sup>4</sup> *Ber. d. Chem. Ges.*, 20, 414.

clusion that the  $\alpha$  hydropiperic acid was a  $\beta \gamma$  unsaturated acid, and that the  $\beta$  hydropiperic acid must be an  $\alpha \beta$  unsaturated acid.

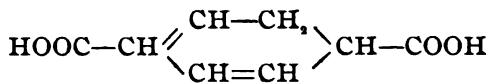
Therefore, by the conversion of the  $\alpha$  hydropiperic acid into the  $\beta$  hydropiperic acid, under the influence of hot caustic soda, a moving of the double bond of union towards the carboxyl group takes place as follows:



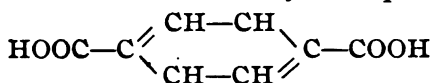
Other such displacements of the double bonds of union through the agency of alkalis and even by boiling water were soon found. Baeyer<sup>1</sup> observed, that the  $\delta^{2,5}$  dihydroterephthalic acid, became the  $\delta^{1,5}$  dihydroterephthalic acid, when boiled with water, and the latter, in turn, when boiled with caustic soda, produced the  $\delta^{1,4}$  dihydroterephthalic acid, according to the following scheme:



$\delta^{2,5}$  dihydroterephthalic acid.



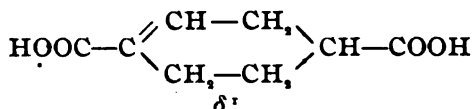
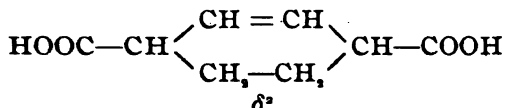
$\delta^{1,5}$  dihydroterephthalic acid.



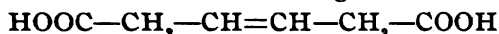
$\delta^{1,4}$  dihydroterephthalic acid.

Further  $\delta^2$  tetrahydroterephthalic acid when treated with hot caustic soda produces  $\delta^1$  tetrahydroterephthalic acid as follows:

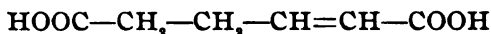
<sup>1</sup> *Ann. Chem.*, 251, 257,



Finally hydromuconic acid according to Baeyer and Rupe<sup>1</sup> by the same treatment is changed into an isomeric  $\alpha \beta$  acid, as:



$\beta \gamma$  hydromuconic acid.



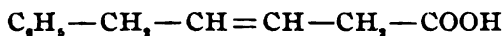
$\alpha \beta$  hydromuconic acid.

Even previous to this Fittig<sup>2</sup> had been led to the conclusion, that in the potassa-fusion of hydrosorbic acid a moving of the double union from the  $\beta \gamma$  to the  $\alpha \beta$  position must also take place, since the splitting, thereby occasioned, occurs at the  $\alpha \beta$  position with the production of butyric and acetic acids, still the hydrosorbic acid is unquestionably a  $\beta \gamma$  unsaturated acid, which, therefore, must split into two molecules of propionic acid.

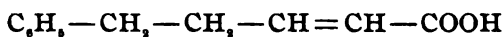
All these observations but favored the belief, that the shoving of the double union in the unsaturated acids towards the carboxyl group when boiled with caustic soda was a general one.

To prove the correctness of this point, Fittig began with his pupils, on a series of  $\beta \gamma$  unsaturated acids, and in all the researches as yet made, no exception has been found. Of the aromatic acids, aside from hydropiperic acid the following have been examined:

Phenyl  $\beta \gamma$  pentinic acid, which gives, according to T. Hoffmann, with boiling caustic soda, the isomeric phenyl  $\alpha \beta$  pentinic acid.



$\beta \gamma$

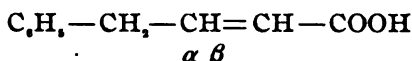
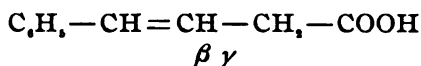


$\alpha \beta$

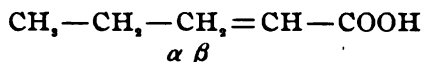
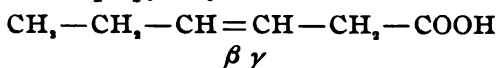
<sup>1</sup> Ibid, 256, 1.

<sup>2</sup> Ibid, 255, 13.

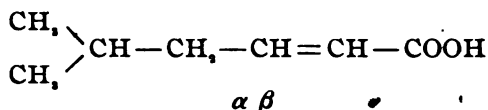
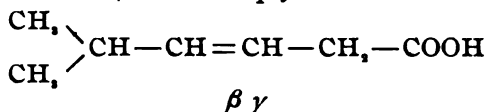
Phenylisocrotonic acid is changed, after Luib, by a like treatment into benzylacrylic acid.



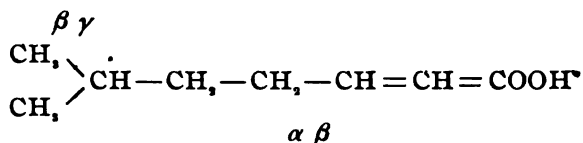
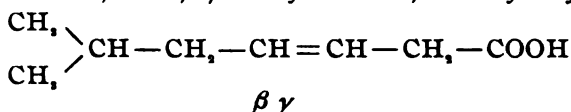
In the "fatty series" this change takes place regularly. Baker obtained from hydrosorbic acid by boiling with caustic soda  $\beta$  propylacrylic acid.



Feurer, from isoheptylic obtained isobutylacrylic acid.



Weill, from  $\beta \gamma$  isocytic the  $\alpha \beta$  isoamylacrylic acid.



The present work was taken up with a view of extending these researches by including acids of the " $\gamma \delta$  series."

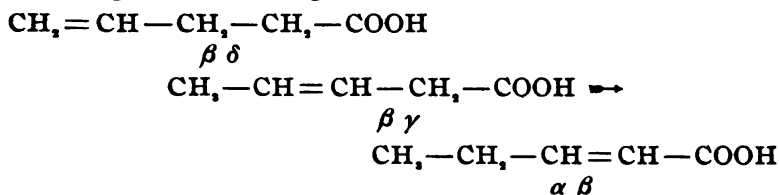
The supposition of Zincke and Kuester<sup>1</sup> that the  $\gamma \delta$  unsaturated acids would, when boiled with caustic soda, also allow of a displacement of their double bonds, can be given as one of the principal reasons for beginning the investigations.

If the supposition of Zincke and Kuester is correct, then the following, which they looked upon as very probable, would

<sup>1</sup> Ber. d. chem. Ges., 24, 909.



have been most interesting: that is, if the  $\gamma \delta$  acids should suffer their double bond to be moved, then it would be an easy matter to produce a  $\beta \gamma$  and in turn an  $\alpha \beta$  acid, for example, from allylacetic acid, ethylidenepropionic acid, and finally propylideneacetic acid should be obtained by boiling with caustic soda, according to the following:



The first part of this paper is taken up in the description of the results of the experiments, on two  $\gamma \delta$  acids, allylmalonic and allylacetic acids.

In the case of both of these acids, the following surprising results were obtained. On boiling with caustic soda no conversion into the corresponding  $\beta \gamma$  and  $\alpha \beta$  unsaturated acids could be detected. This passive behavior, of both of these representatives of the " $\gamma \delta$  series," is, therefore, the more remarkable, since from analogy, taken from the already observed inclination of terminal methylene radicals, to form methyl groups, as for instance, Faworsky<sup>1</sup> found in the unsaturated hydrocarbons, a complete change might be expected here. On the other hand Baeyer<sup>2</sup> has verified these exceptions to Faworsky's rule in the case of the hydrated phthalic acids.

Finally, if this difference to boiling caustic soda should be asserted in other  $\gamma \delta$  acids and become a general characteristic of this series, then through this means a sharp and decided distinguishing property has been discovered between the  $\gamma \delta$  and the  $\beta \gamma$  unsaturated acids, which, moreover, behave alike in the substitution of hydrobromic acid and the decomposition of the product, by means of water and alkalis (Messerschmidt<sup>3</sup>); as also in the substitution of bromine (Urban<sup>4</sup>); and in the treatment with potassium permanganate (Urban<sup>5</sup>).

The second part of this research is given to a description of the

<sup>1</sup> *J. prakt. Chem.*, 44, 212.

<sup>2</sup> *Ann. Chem.*, 269, 150.

<sup>3</sup> *Ibid.*, 208, 93.

<sup>4</sup> *Ibid.*, 268, 60.

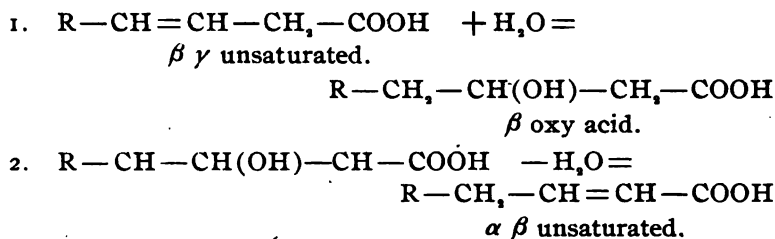
<sup>5</sup> *Ibid.*, 268, 32.

results obtained in the treating with caustic soda the  $\beta \gamma$  acid corresponding to allylacetic acid, that is, ethyldenepropionic acid.

As a result it was found that this  $\beta \gamma$  unsaturated acid, like all the others, which have as yet been investigated, on boiling with caustic soda, allowed the double union to be shoved to the  $\alpha \beta$  position, with the formation of propylideneacetic acid, formerly known, but until now only in the impure state.

Even from the first, investigators on the moving of the double bond of union, through the influence of boiling caustic soda, busied themselves with efforts to explain the mechanism of the reaction.

Based on analogous reactions Weinstein<sup>1</sup> suggested that by warming the  $\beta \gamma$  unsaturated acids with caustic soda the elements of water are taken up and an oxy acid formed, and this in turn, giving it up again, an  $\alpha \beta$  unsaturated acid results, as follows:



This meanwhile purely hypothetical  $\beta$  oxy acid, forms, therefore, the intermediate step between the two isomeric unsaturated acids.

Although Weinstein himself could not isolate this oxy acid still it has been formed repeatedly since then, thus:

Luib obtained from phenylisocrotonic acid phenyl  $\beta$  oxybutyric acid  $C_6H_5-CH_2-CH(OH)-CH_2-COOH$ .

Hoffmann from phenyl  $\beta \gamma$  pentinic acid produced phenyl  $\beta$  oxyvalerianic acid.



However, just through Hoffmann's careful investigations, the idea that the  $\beta$  oxy acid was the middle link, in the change

<sup>1</sup> *Ann. Chem.*, 227, 31.

from the  $\beta \gamma$  unsaturated, to the  $\alpha \beta$  acids was made somewhat doubtful.

He found for example that the  $\beta \gamma$  acid after six hours boiling with caustic soda gave fifty per cent. of  $\alpha \beta$  acid without any trace of  $\beta$  oxy acid, and that further, the formation of the oxy acid required a very long and protracted treatment with the alkali, and that finally, the  $\beta$  oxy acid can be most easily produced, by boiling the  $\alpha \beta$  acid with caustic soda. Briefly, his observations leave the impression as if the  $\beta$  oxy acid is not the intervening middle link between  $\beta \gamma$  and  $\alpha \beta$  acids, but is a secondary one to, and resulting from the  $\alpha \beta$  acid.

In the "fatty series," on the contrary, the reaction seems to follow the course of the above scheme of Weinstein even if it has certain restrictions.

Baker's work pointed to, and Feurer's observations made it certain, that the three acids which he examined  $\beta \gamma$  isohexylylic,  $\beta$ oxydimethylvalerianic, and  $\beta$  isobutylacrylic acids, when boiled with caustic soda, gave certain quantities of both of the others; the reaction does not, however, proceed smoothly in every sense of the term, but only to a certain limit, the  $\beta$  oxy acid always forming the intermediate product of the two unsaturated isomers.

These observations also cover the results described in the second part of this paper, they having been also noticed in the examination of the  $\beta$  oxy valerianic acid obtained from ethylidenepropionic acid.

#### PART I.

*On the behavior of allylmalonic and allylacetic acids when boiled with caustic soda solutions.*

#### PART II.

*On the behavior of ethylidenepropionic acid when boiled with caustic soda.*

*Contributions to the knowledge of propylideneacetic acid.*

#### PART I.

*Preparation of Allylmalonic Acid.*—The allylmalonic acid was produced according to Conrad and Bischoff,<sup>1</sup> from malonic acid, ethyl ester, and allyl iodide.

<sup>1</sup> *Ann. Chem.*, 204, 168.

The malonic acid ethyl ester was obtained from Claisen and Crismer's<sup>1</sup> modification of Conrad's<sup>2</sup> method; the allyl iodide in turn was prepared after Kannonikoff and Saytzev<sup>3</sup> and Wagner's<sup>4</sup> improved suggestions of Berthelot and Luca.<sup>5</sup>

Since the purity of the allylmalonic acid depends principally on the absolute purity of the allyl iodide, a few precautionary hints, which have recommended themselves during the course of preparation, may not be amiss here.

1. Some ignited sand was put into the retort, thereby overcoming, on the one hand, the danger of breaking the latter through the phosphorus or iodine becoming attached to the bottom of the retort, and on the other, the action of the phosphorus is rendered more uniform and regular.

2. The retort was filled to one-half or at least one-third of its capacity.

3. It is particularly desirable that the phosphorus react directly as it is brought into the retort and that the allyl iodide distill over at once; this is facilitated by covering the upper part of the bowl and beak of the retort with a cloth to guard against cooling.

If the allyl iodide is not carried over as soon as formed, then much isopropyl iodide is produced, which is only with the greatest difficulty separated from the allyl iodide. Through repeated careful fractional distillations a preparation boiling between 99° and 102° C. and possessed of only a light-red color, was obtained.

To prepare the allylmalonic acid ester, the allyl iodide was run as rapidly as possible into the well-cooled sodium malonic acid ester and the product obtained after two hours boiling, separated by shaking with ice-water, and fractioning without further drying. The fractions were collected at every 5° from 150° to 200°, and at every 2° from 200° to 235° C.

After repeated and successive fractioning the four portions from 218° to 226° were taken to be pure and so used.

The saponification of the ester, which Conrad and Bischoff<sup>6</sup> performed with potassium hydroxide was in this case accomplished with barium hydroxide, in which the four fractions from

<sup>1</sup> *Ibid.*, 218, 131.

<sup>2</sup> *Ibid.*, 204, 131.

<sup>3</sup> *Ann. Chem.*, 185, 191.

<sup>4</sup> *Ber. d. chem. Ges.*, 9, 1810.

<sup>5</sup> *Ann. Chem.*, 204, 168.

<sup>6</sup> *Ann. Chem.*, 204, 168.

218° to 226° were separately treated. After the saponification was complete, the contents of the flask were diluted with hot water and the excess of barium hydroxide removed by means of carbonic acid gas; it was now filtered, and the filtrate evaporated to obtain the crystalline barium allylmalonate in fractions, the several crystallizations of the original fractions being held separate, until the subsequent decomposition by means of hydrochloric acid proved them to be pure.

Thanks, to this careful and protracted process of fractioning, a white, almost perfectly pure acid was obtained, from which through the aid of the acid barium salt, an absolutely pure acid melting at 105° C. was prepared. The production of pure acid amounted to thirty-three per cent. of the theory.

*Boiling Allylmalonic Acid with Caustic Soda Solution.*—Two experiments were performed.

In the first one, ten grams of pure allylmalonic acid were boiled for twenty hours (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary for neutralization in a ten per cent. aqueous solution. Allowed to cool, the alkaline liquid was strongly acidified with sulphuric acid and shaken out with ether; after distilling off the ether a faintly yellow-colored oil remained behind, hardening to a white crystalline mass in a vacuum over sulphuric acid, and melting at 103° C. when crystallized out of benzene; after being purified by means of the acid barium salt the melting-point was raised to 105° C.; the substance was, therefore, pure and unaltered allylmalonic acid; it represented 9.591 grams or 95.9 per cent. of the acid originally used.

In the second test 7.3305 grams of allylmalonic acid were boiled in the same manner for twenty hours with a twenty per cent. solution of caustic soda representing ten times the necessary amount of alkali for neutralization; allowing to cool, acidifying, shaking out with ether, recrystallizing out of benzene, and purifying by means of the acid barium salt, 7.1345 grams of pure allylmalonic acid melting at 105° C. was recovered, corresponding to 97.3 per cent. of the amount used.

The loss of four and one-tenth per cent. in the first and two and seven-tenths per cent. in the second is explained by the fact

that it is impossible to recover the last portions of the acid from its solutions by means of ether.

The identity of the acid obtained, with allylmalonic acid, was not only proven by the melting-point, but also by other physical properties, as also by its deportment on distillation.

*Preparation of Allylacetic Acid.*—Zeidler<sup>1</sup> first obtained allylacetic acid from allylacetic acid ester and dry sodium ethylate, and stated its boiling-point to be 182° C. Conrad,<sup>2</sup> who got it by distilling allylmalonic acid, found the boiling-point to be 184° C.

According to Messerschmidt,<sup>3</sup> who used a modification of Zeidler's method, it boiled at 187° to 189° C.

Finally Marburg<sup>4</sup> studied the acid obtained by means of the Conrad as well as the Zeidler-Messerschmidt methods in both their physical and chemical properties and definitely settled the boiling-point at 186° to 187° C.

The allylacetic acid used in these researches was made after Conrad's process; it boiled constantly at 186° to 187° C. The production was about sixty-two per cent. of the theory.

*Boiling of Allylacetic Acid with Caustic Soda Solution.*—Ten grams of pure allylacetic acid boiling at 186° to 187° C. was boiled (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary to neutralize it, in ten per cent. solution for twenty hours.

The cold contents of the flask were then strongly acidified with sulphuric acid and shaken out with ether, after distilling off the latter the residual acid was distilled with steam.

According to the statement given in the beginning of this paper one must consider the presence of  $\beta$   $\gamma$ , and  $\alpha$   $\beta$ , as well as of an oxy acid, and the use of steam was considered the better means of effecting their separation.

The distillation was continued until the distillate reacted neutral, the residual liquid in the distillation flask being then shaken out with ether; by this latter process nothing could be extracted; no oxy acid had, therefore, been formed.

The aqueous distillate was neutralized with barium carbonate

<sup>1</sup> *Ann. Chem.*, 187, 4.

<sup>2</sup> *Ibid*, 204, 170.

<sup>3</sup> *Ibid*, 208, 93.

<sup>4</sup> Dissertation, Strassburg, 1887.

in the cold, boiled, filtered, and evaporated to dryness; in this manner 15.85 grams of barium salt dried at  $100^{\circ}$  was obtained. The finely powdered salt was repeatedly extracted with hot absolute alcohol, thereby one and a half grams dissolved, remaining as an amorphous yellow-colored transparent mass, upon distilling off the alcohol. Redissolved in alcohol and allowed to evaporate in a desiccator it was again deposited amorphous. This experiment gave, therefore, 90.5 per cent. of barium salt insoluble in alcohol.

In order to obtain a larger amount of the soluble salt a second trial was begun under the same conditions as the first with ten grams of allylactic acid; it gave 16.52 grams of dry barium salt of which one gram was soluble in hot alcohol leaving ninety-four per cent. undissolved. The two portions of insoluble barium salt were mixed, and a careful fractional crystallization begun. This process allowed of the eventual separation of the  $\beta$   $\gamma$  and  $\alpha$   $\beta$  acids from the barium allylacetate. To this end the salt was dissolved in the least possible amount of hot water, filtered, evaporated to a pellicle, and allowed to crystallize.

The first crystals obtained were flat and lanceolate prisms, later flat curved needles and leaves were shot out; an easily soluble salt could, however, not be detected.

The difference in appearance of the crystals would not necessarily point to the presence of different salts, since, on the one hand, pure barium allylacetate separates out in entirely different forms according as it crystallizes out more rapidly or slowly, and on the other hand, the last fractions could, when dissolved in water, adding alcohol until precipitation began, warming and then allowing to cool slowly, be obtained in small needle-shaped crystals of exactly the same appearance.

To examine the acid the several crystallizations together with their mother-liquors were mixed, the alcohol distilled off, and the organic acid set free and removed by successive treatments with hydrochloric acid and ether, the ethereal solution shaken with calcium chloride, filtered, and distilled from a small flask, the principal portion passed over from  $186^{\circ}$  to  $187^{\circ}$  C., a higher boiling fraction not occurring.

Because the barium salt had lost considerable in weight in

the successive evaporations (due to a slight decomposition) a third trial of boiling the allylacetic acid with caustic soda was made, in order to exclude any doubt of its conversion into  $\beta$   $\gamma$  or  $\alpha$   $\beta$  acid.

13.65 grams of allylacetic acid boiling at  $186^{\circ}$  to  $187^{\circ}$  C. and which had been recovered from former trials, were boiled with twenty per cent. sodium hydroxide for twenty-two hours, in the same manner as the others had been; also here the ether extract was entirely volatile, leaving no trace of an oxy acid.

The aqueous acid distillate was made slightly alkaline with sodium carbonate, evaporated to dryness, the sodium salt so obtained decomposed with sulphuric acid and extracted with ether. The ethereal extract was dried and gave 11.96 grams of an acid boiling at  $186^{\circ}$  to  $187^{\circ}$  C.; portions of a higher boiling-point were not present.

To more closely characterize the distillate 2.96 grams of the fraction boiling at  $186^{\circ}$  to  $187^{\circ}$  C., were subjected to the well-known "Lactone Reaction." For this purpose the acid was mixed with five times its weight of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume water) in a small flask and heated just to boiling for fifteen minutes with constant agitation. The organic acid, which at first swam on the surface of the mixture, soon dissolved with a yellow coloration of the liquid; the contents of the flask was diluted with an equal volume of water and boiled for fifteen minutes, then cooled and extracted with ether.

The ethereal extract was dissolved in a little water, made slightly alkaline with sodium carbonate and at once shaken out with ether, a yellow-colored neutral liquid resulting, which, after drying, boiled constantly at  $206^{\circ}$  C., proving it to be pure valerolactone produced from the unaltered allylacetic acid.

The alkaline solution freed from lactone was, after removing the ether, acidified with sulphuric acid and distilled with steam; the distillate after neutralizing with calcium carbonate, filtering, and evaporating to dryness gave 0.1352 gram of a gray residue equivalent to 4.57 per cent. of the acid used.

From these three trials one can certainly conclude that by boiling allylacetic acid with caustic soda, neither propylidene-



acetic acid, nor ethylidenepropionic acid, nor an oxy acid is formed in any quantity, which can be detected.

If a change does at all occur it is almost imperceptible. The small quantities of a barium salt soluble in alcohol were not sufficient to settle the question, whether it was the salt of the  $\alpha$   $\beta$  acid.

## PART II.

The ethylidenepropionic acid,  $\text{CH}_3\text{—CH=CH—CH}_2\text{—COOH}$  was prepared according to Fraenkel<sup>1</sup> by the distillation of methylparaconic acid.

*Preparation of Methylparaconic Acid.*—Methylparaconic acid was first made by Gantter<sup>2</sup> from acetosuccinic acid ester, by reducing with sodium amalgam and described under the name of ethylidene hydroxysuccinic acid. Fraenkel,<sup>3</sup> however, was the first one who obtained it pure; he prepared it by the condensation of acetaldehyde with sodium succinate; he also described it more closely.

The acid used in the present research was prepared according to Gantter's method, and since the preparation is somewhat difficult it may not be amiss to give it more than a casual description here.

1. Monochloracetic acid ester, was obtained after the Conrad<sup>4</sup> process; it gave a yield of eighty-five per cent. of the theoretical amount.

2. The acetosuccinic acid ester, was prepared according to Conrad's<sup>5</sup> process, which by fractioning under reduced pressure gave upwards of sixty per cent. of the theory.

In the acetosuccinic acid ester synthesis, it is of advantage to add the acetic acid ester, as well as the monochloracetic acid ester as rapidly as possible through a stoppered funnel into a flask containing the sodium ethylate and connected with a return condenser; by so doing the violent bumping of the contents of the flask is prevented; this can only otherwise be accomplished by filtering off the sodium chloride, which separates out in the reaction.

After the two esters have been brought together, the contents

<sup>1</sup> *Ann. Chem.*, 255, 24.

<sup>2</sup> Dissertation, Wuerzburg, 1878.

<sup>3</sup> *Ibid*, 255, 18.

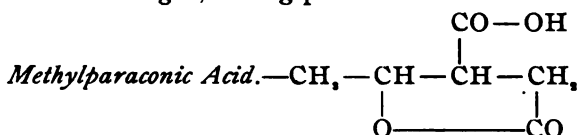
<sup>4</sup> *Ibid*, 188, 218.

<sup>5</sup> *Ann. Chem.*, 188, 218.

of the flask are kept boiling on the water-bath for two hours, allowed to cool, mixed with ice-water, and extracted with ether; a reddish-brown crude ester is obtained, which, after being shaken with small portions of water, is subjected to fractional distillation. Drying by the use of calcium chloride is not to be recommended, since the salt dissolves, and when distilled, causes a decomposition of the ester, as Gottstein<sup>1</sup> and Young<sup>2</sup> have also observed in similar esters.

To free the crude ester of ether, alcohol, water, unaltered acetic acid ester, and monochloroacetic acid ester, it was heated to 200° C. That portion, which did not distill off at this temperature, was then fractioned in a rarefied atmosphere under fifty mm. pressure and this repeated three times, gave an ester boiling at 180° to 183° C.

This was accepted as pure acetosuccinic acid ester; it presented a colorless pleasant smelling liquid almost as thick as glycerol. By fractioning under the ordinary pressure it was never found possible to obtain an ester as colorless, nor boiling as constantly, and notwithstanding the statements of Conrad<sup>3</sup> it is the author's opinion that it can not be distilled under ordinary pressure even when perfectly pure, without a decomposition more or less slight, taking place.



Pure acetosuccinic acid ester, in portions of twenty-five grams each, was mixed with a like quantity of absolute alcohol, and water added to a turbidity, then four per cent. sodium amalgam was added, the vessel being frequently agitated. At the beginning the sodium amalgam melted in a short time without any perceptible evolution of gas; when the reaction diminished in consequence of the concentration of the liquid more water was added until turbidity again appeared and the reaction renewed.

The mercury resulting from the decomposition of the amalgam was taken out from time to time with a pipette, washed with water, and the wash-water added to the original reducing fluid.

<sup>1</sup> Ibid, 216, 31-36.<sup>2</sup> Ibid, 216, 43.<sup>3</sup> Ann. Chem., 188, 218.

The latter was, during the process of reduction, neutralized with dilute sulphuric acid to prevent the accumulation of a large excess of alkali. The entire process was continued until three times the theoretical amount of sodium amalgam had been added.

It is necessary in the reduction to observe that the solution does not become too warm (for this reason it may be well to set the vessel containing it, into ice-water at the beginning), also that it does not become too alkaline, otherwise a splitting of the acetosuccinic acid ester can easily occur, which, according to Wislicenus,<sup>1</sup> can follow in two directions.

When the sodium amalgam had ceased to act the liquid was, after removing and washing the mercury, exactly neutralized with dilute sulphuric acid, filtered, evaporated to a small volume, and allowed to crystallize, the mother-liquor drained off from the crystals of sodium sulphate, acidulated with sulphuric acid, and extracted with ether; the ethereal residue at first a yellow oil, soon becomes a solid mass when placed in a vacuum over sulphuric acid. This solid mass relieved of the oily matters by suction with a filter pump and pressure between bibulous paper gave, when broken into small pieces and kept over sulphuric acid in a vacuum, a perfectly dry white powder; this was the desired methylparaconic acid.

It was crystallized out of benzene in the following manner: A flask containing the powdered acid and some benzene, and fitted with a perforated cork, through which passed a long glass tube, was heated by plunging it into boiling water, it being constantly agitated, so as to bring the now melted underlying acid into intimate contact with the supernatant solvent; allowed to settle, and the clear solution decanted (from the liquid and still undissolved acid) into flasks, which were at once stoppered and set aside to crystallize. To the still undissolved acid in the first flask more benzene was added and the same process continued until no more was dissolved.

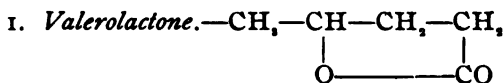
If before being dissolved in the benzene the acid was perfectly dry and therefore free from all oily matters then it dissolves completely and crystallizes out in hard dry crystals; if, however,

<sup>1</sup> Ibid, 190, 275.

*Preparation of Ethylidenepropionic Acid.*—The ethylidenepropionic acid was made according to Fraenkel.<sup>1</sup> Pure methylparaconic acid, in portions of fifteen grams each, was carefully heated in a small distillation flask; at first the acid melted to a colorless fluid, but took on a yellowish-red coloration as the operation advanced. When the temperature of the molten acid had reached 200° C. a slight evolution of carbon dioxide had begun and as the immersed thermometer indicated 240° to 260° C. the evolution of gas was a very regular one.

The thermometer bulb was now drawn up to the opening of the exit tube and the distillation continued to the end, the vapors passing over at  $210^{\circ}$  to  $220^{\circ}$  C. A slight carbonaceous residue representing nine-tenths per cent. of the acid used, alone remained behind.

1. Valerolactone.
2. Ethylidenepropionic acid.
3. Methylcitraconic acid.
4. Methylitaconic acid, and
5. Unaltered Methylparaconic acid.



The empyreumatic distillate, mixed with five times its volume of water, was made slightly alkaline with sodium carbonate in the cold, and rapidly extracted with ether; a reddish-yellow oil resulted, which, after removing the ether and water, could be easily characterized as valerolactone.

<sup>1</sup> *Ann. Chem.*, 255, 24.

2. *The Acids.*—The alkaline solution, from which the lactone had been extracted, was acidulated with sulphuric acid and completely extracted with ether; the acid mixture so obtained was distilled with steam until the distillate ceased to be acid. The slightly turbid distillate was made faintly alkaline with barium hydroxide, treated with carbonic acid gas, boiled, and filtered; in this manner a solution of barium ethylidenepropionate and methylcitraconate was obtained, which can be separated by fractional crystallization.

The acid residue left in the distillation flask after distilling with steam, was evaporated to a small bulk, when it solidified to a yellow crystalline mass on being placed over sulphuric acid in a vacuum.

By treating this mass with cold chloroform the unaltered methylparaconic acid was easily extracted, while the methylitaconic acid, which was present only in small quantities, remained undissolved as a powder; the latter, like the methylcitraconic acid, was not used further.

To separate the barium methylcitraconate from the barium ethylidenepropionate, the solution containing both was simply evaporated when the barium methylcitraconate difficultly soluble in the heat separated out; it was then filtered again, evaporated, and so continued until no more salt difficultly soluble in the heat, separated out. The mother-liquors deposited upon further evaporation, when cold, the barium ethylidenepropionate in the form of flat lanceolate prisms grouped together into stars. To remove every trace of barium methylcitraconate, the barium ethylidenepropionate was recrystallized three times. It was then exactly decomposed with a weak solution of sodium sulphate, and thereby, after filtering and evaporating, sodium ethylidenepropionate obtained, in which form it was later mostly used.

200 grams of methylparaconic acid gave about forty-five grams, or twenty-two and one-half per cent. of ethylidenepropionic acid.

*Preparation of Propylideneacetic Acid.*—By the action of propionaldehyde on malonic acid Komnenos<sup>1</sup> obtained a monobasic unsaturated acid with five atoms of carbon, which he called pro-

<sup>1</sup> *Ann. Chem.*, 218, 166.

pylideneacetic acid. In the same manner Zincke and Kuester,<sup>1</sup> as well as Ott<sup>2</sup> and Viefhaus,<sup>3</sup> prepared their propylideneacetic acid.

Zincke and Kuester<sup>4</sup> also obtained, in an entirely different manner, an acid which they recognized to be identical with Komnenos's propylideneacetic acid.

Starting with hexachlordiketo R hexane obtained from catechol, orthoamidophenol and chlorine they prepared successively tetrachlorcatechol or tetrachloramidophenol, and then pentachlorbutane carbon dioxide, and by treating the latter with sodium amalgam, procured their acid.

Fittig and Fraenkel,<sup>5</sup> however, suspected that the above acid of Zincke and Kuester was identical with ethylidenepropionic acid, obtained from methylparaconic acid; this supposition was, through the later researches of Zincke and Kuester,<sup>6</sup> made very probable, inasmuch as these investigators obtained small quantities of lactone by treating the bromhydric acid addition product of their acid with water, from which it would appear that the acid must be ethylidenepropionic acid or at least contain it as an impurity, since pure propylideneacetic acid can produce no lactone.

Such acids as have been prepared and described under the name of propylideneacetic acid are no homogeneous bodies. It was not until the writer, in July, 1892, procured the acid in its crystalline form by boiling ethylidenepropionic acid with caustic soda; and Mackenzie,<sup>7</sup> in February, 1893, secured it after the method of Komnenos that pure propylideneacetic acid had been made and characterized.

*Boiling of Ethylidenepropionic Acid with Sodium Hydroxide.*—Sodium ethylidenepropionate, in portions of ten grams each, was boiled with thirty-three grams of sodium hydroxide dissolved in 295 grams of water for fifteen hours in a copper flask connected with a return condenser. The cold alkaline solution was now acidulated with ether, the ethereal extract distilled with steam until the distillate came over perfectly neutral; the milky acid

<sup>1</sup> *Ber. d. chem. Ges.*, 22, 494. *Ibid.*, 23, 818. *Ibid.*, 24, 909.

<sup>2</sup> *Ibid.*, 24, 2,600. <sup>3</sup> *Ibid.*, 26, 915. <sup>4</sup> *Ibid.*, 21, 2,719.

<sup>5</sup> *Ibid.*, 255, 33. <sup>6</sup> *Ber. d. chem. Ges.*, 24, 909.

<sup>7</sup> Dissertation, Strassburg, 1894.

distillate was neutralized with barium carbonate in the cold, filtered, and evaporated to dryness.

From the liquid remaining in the distillation flask the  $\beta$  oxyvalerianic acid was obtained (see  $\beta$  oxyvalerianic acid).

To separate the ethylidenepropionic acid and expected propyldeneacetic acids, the dry barium salt was repeatedly extracted with hot alcohol and filtered hot each time; the barium salt remaining undissolved was perfectly white and proved to be unaltered barium ethylidenepropionate; it was through double decomposition with sodium sulphate changed to the sodium salt, in which form it was again boiled with caustic soda. In the alcohol another barium salt had been dissolved; on distilling off the solvent a light yellow-colored, amorphous varnish-like mass was left behind; this was supposed to be the barium salt of the newly formed  $\alpha \beta$  acid.

To remove every trace of  $\beta \gamma$  acid from it, the barium salt was decomposed with sodium sulphate forming the sodium salt, and this mixed with a quantity of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume of water), corresponding to five times the amount of organic matter present, plus a sufficiency to neutralize the sodium of the sodium salt and heated in a flask almost to boiling, with constant agitation for fifteen minutes, then mixed with a like bulk of water and boiled for thirty minutes. Allowed to cool, the acid solution is extracted with ether, the ethereal extract again rapidly boiled with some water, and a few drops of dilute sulphuric acid to again change into lactone any oxy acid, which may have been formed, rapidly cooled off, sodium carbonate added to an alkaline reaction, and the lactone at once shaken out with ether. The alkaline solution free from lactone was again acidified, extracted with ether, and the ethereal residue distilled with steam, the acid distillate neutralized with sodium carbonate anew, and the sodium salt obtained, again treated with sulphuric acid as above. The entire operation was repeated until no more lactone was formed; this was accomplished after repeating it two or three times, when every trace of  $\beta \gamma$  acid had surely been removed.

Propyldeneacetic acid:  $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{COOH}$ .

After no more lactone could be detected in shaking the alka-

line liquid after boiling with sulphuric acid, the solution was acidified and distilled with steam, and from the acid distillate the sodium or calcium salt of the  $\alpha\beta$  acid produced. On decomposing the sodium salt with sulphuric acid, or the calcium salt with hydrochloric acid in a narrow tube, the pure  $\alpha\beta$  acid was obtained as an almost colorless oily layer; it was drawn off, the last portions extracted with ether, and the ethereal solutions dried by means of dried sodium sulphate or calcium chloride, filtered, and the ether evaporated, leaving a colorless oil, which congeals in a freezing mixture at once and remaining solid indefinitely in ice-water, since it melts at  $7\frac{1}{4}^{\circ}$  to  $8\frac{1}{4}^{\circ}$  C.

In cold winter weather it is extremely easy to obtain the acid perfectly pure and of the correct melting point.

The acid from the ethereal extract is poured into a watch-glass and placed in a desiccator at a low temperature; it then solidifies in flat rhombohedral tables or leaves, which can, with the aid of a cold platinum wire, be brought upon a piece of filter paper, to there give up the last traces of moisture, remaining behind as flat, glistening crystals. The acid is therefore the  $\alpha\beta$  acid, corresponding to the ethylidenepropionic acid; its melting-point, compared with a specimen of the acid subsequently prepared, after the method of Komnenos,<sup>1</sup> which was purified and crystallized in a like manner, gave the following results.

A specimen of each was placed on the bulb of the same thermometer and plunged into a freezing mixture for a minute and then into cold water, the temperature of which was gradually raised.

At  $6\frac{1}{4}^{\circ}$  C. they both remained solid.

At  $7^{\circ}$  C. likewise so.

At  $7\frac{1}{4}^{\circ}$  C. both samples began to melt slightly.

At  $7\frac{1}{2}^{\circ}$  C. both were about half melted.

At  $8^{\circ}$  C. only a small quantity of each still remained solid.

At  $8\frac{1}{4}^{\circ}$  C. both were completely melted.

The melting-point determinations were made by placing the acid in thin-walled melting-point tubes two mm. in diameter, and closed at both ends; this allowed of a repetition of the esti-

<sup>1</sup> *Ann. Chem.*, 218, 166.



mations without any danger of loss by evaporation or inaccuracy from the absorption of water.

During some recent work on propylideneacetic acid by the Komnenos' process, Mackenzie<sup>1</sup> found the melting-point to be  $9\frac{1}{4}^{\circ}$ – $10\frac{1}{4}^{\circ}$  C.

It is much more difficult to obtain the solid acid of a constant melting-point in summer; to this end the following method was used: The acid freed, as much as possible, from ether and water, contained in a small flask held horizontally, was moved backwards and forwards through a water-bath of  $65^{\circ}$  C., in order to remove the last traces of ether. The flask was then closed with a stopper and calcium chloride tube, and plunged into a freezing mixture of ice and salt, in such a manner that the acid congeals on one side of the flask; the flask was now placed upright in a vessel of ice-water for an hour; the mother-liquor draining out was poured off; finally the crystalline cake was itself slightly warmed, so that the last low melting portions of the acid percolated out what remained congealed in a freezing mixture completely and did not remelt in ice-water.

Pure propylideneacetic acid becomes solid at  $0^{\circ}$  C.; if the melted acid be placed in ice-water, it solidifies in half an hour. If a crystal of the acid be dropped in, it congeals at once. The smallest quantities of water or ether have a decided effect on its melting-point.

At the ordinary temperature pure propylideneacetic acid is a mobile colorless liquid with a faint, pleasant odor of acetic acid. It is so volatile, that even at  $45^{\circ}$  C. it passes over with the ether vapors, and in summer a considerable loss is not to be prevented when working with this substance.

About sixty per cent. of the ethylidenepropionic acid is converted into propylideneacetic acid by boiling with caustic soda. For analysis the acid melting at  $7\frac{1}{4}^{\circ}$  to  $8\frac{1}{4}^{\circ}$  C. was used.

1. 0.2716 gram acid gave 0.1915 gram  $H_2O$ , and 0.595 gram  $CO_2$ .

2. 0.2965 gram acid gave 0.2125 gram  $H_2O$ , and 0.6508 gram  $CO_2$ .

<sup>1</sup> Dissertation, Strassburg, 1894.

	Calculated for $C_6H_8O_4$ .	Found.	
C .....	60.00	59.75 per cent.	59.86 per cent.
H .....	8.00	7.84 " "	7.96 " "

*Salts of Propylideneacetic Acid.*—Barium Salt. The barium salt of propylideneacetic acid is very characteristic; it was prepared by neutralizing propylideneacetic acid with barium carbonate suspended in water; the neutral solution was boiled, filtered, and evaporated to a pellicle; after cooling, the pellicle was removed from the surface of the solution and the liquid placed in an ice-chest (for when allowed to evaporate at the ordinary temperature a sticky mass only separates out) to undergo a very slow evaporation. After some weeks the salt is deposited in needles grouped to rosettes; these were washed and subjected to analysis.

The salt contains considerable water of crystallization, but effloresces easily, becoming anhydrous in a desiccator over sulphuric acid.

1. The salt pressed between filter paper and allowed to remain in an ice-chest on a piece of filter paper over night, was on the following morning weighed into an open crucible, and allowed to remain in a desiccator to constant weight.

0.2102 gram lost 0.0170 gram  $H_2O$  or 8.10 per cent.

2. The pressed salt was, after remaining for fifteen minutes on a piece of filter paper in the ice-chest, weighed into an open crucible and allowed to remain to constant weight in a desiccator.

0.6470 gram lost 0.1028 gram  $H_2O$  or 15.88 per cent.

3. The pressed salt was placed for twenty-five minutes in the air at  $14^\circ C.$  and then treated as above.

0.2493 gram lost 0.0203 gram  $H_2O$  or 8.14 per cent.

4. 0.1932 gram of the salt dried in a desiccator gave 0.1335 gram  $BaSO_4$ , 0.0785 gram Ba.

Calculated for $(C_6H_7O_4)_2 Ba$ .	Found.
40.89 per cent. Ba.	40.63 per cent. Ba.

It follows from these determinations that because of the disposition of this salt to effloresce, it is impossible to make an exact estimation of the water; the difference in amount seems to depend on the temperature at which the crystallization takes place.

It was found impossible to examine the crystals optically; one can only see that they are tables with end faces, but to which system they belong can not be said.

To observe the deportment of the crystallized salt at a higher temperature, a portion which had crystallized out in the ice-chest was placed together with its mother-liquor in a stoppered vessel and allowed to remain several days at a temperature of 20° C.; a part of the crystals were thereby dissolved; the other portion, however, remained crystalline and did not become sticky.

**Calcium Salt.** The calcium salt was made by neutralizing an aqueous solution of the acid with calcium carbonate in the cold; the solution boiled, filtered, and evaporated to a pellicle; on cooling, the salt crystallized out in moderately long, flat, glistening prisms; they were collected on a platinum cone, washed, dried, and laid on filter paper for twelve hours at 6° C. The salt gives off all its water of crystallization in a desiccator.

0.4155 gram gave 0.0985 gram  $H_2O$ .

Calculated for  $(C_8H_7O_2)_2, Ca+4H_2O$ .

23.22 per cent.  $H_2O$ .

Found.

23.71 per cent.

0.2263 gram of salt dried at 100° C. gave 0.1298 gram  $CaSO_4$ .

Calculated for  $(C_8H_7O_2)_2, Ca$ .

16.81 per cent.  $Ca$ .

Found.

16.87 per cent.  $Ca$ .

The calcium salt crystallizes much easier than the barium salt, since it can be obtained at a temperature of 16° C. in nice prisms, while the barium salt always becomes sticky at this temperature. Calcium propylideneacetate like the barium salt is easily soluble in water and alcohol.

*Propylideneacetic acid dibromide.*

$\alpha$   $\beta$  dibromvalerianic acid.

$\alpha$   $\beta$  pentinic acid dibromide.

$CH_3-CH_2-CHBr-CHBr-COOH$ .

To further characterize the acid, the bromine and bromhydric acid addition products were made.

To prepare the dibromide, the vessels and reagents used were carefully dried.

The acid was dissolved in a little carbon disulphide and then with exclusion of air the calculated amount of bromine in a ten per cent. carbon disulphide solution was added through a drop-

per funnel-tube. A violent reaction was not noticed even at the commencement, the decolorization being slow and incomplete. The experiment was conducted in diffused daylight.

After a small excess of bromine had been added, the whole was cooled off and allowed to remain quiet for twenty-four hours; the most of the carbon disulphide was then removed by aspirating a current of dry air through the bottle; the remaining solution was placed on a large watch-glass in a desiccator, and the disulphide entirely removed by frequent stirring with a glass rod. The desiccator placed in a refrigerator soon caused the dibromide to crystallize out in large leaves.

After the disulphide had been completely removed by alternate stirring, and evacuation of the desiccator, the solid dibromide was dissolved in the least possible quantity of petroleum ether, and the solution allowed to stand in a corked test-tube for several hours. Here the dibromide was deposited in rosettes of flat prisms on the sides of the tube. The mother-liquor was rapidly decanted and the crystals washed two or three times with cold ( $0^{\circ}$  C.) petroleum ether, and again crystallized out of the latter, when the preparation was considered pure.

The dibromide seems not adapted for crystallographic study; the crystallization is probably monosymmetric; it melts without coloration at  $56^{\circ}$  C.; it is very soluble in carbon disulphide and benzene; in petroleum ether it is easily soluble.

0.2040 gram of the dibromide dried in a vacuum gave 0.2957 gram of  $\text{AgBr} = 0.1258$  gram Br.

Calculated for  $\text{C}_8\text{H}_8\text{Br}_2\text{O}_2$ .  
61.54 per cent. Br.

Found.  
61.68 per cent. Br.

$\beta$  Bromvalerianic acid.  $\text{CH}_3 - \text{CH}_2 - \text{CHBr} - \text{CH}_2 - \text{COOH}$ .

The hydrobromic acid addition product of propylideneacetic acid was prepared as follows: To one volume of the pure acid contained in a small cylinder having a well-ground stopper, one and a half volumes of hydrobromic acid saturated at  $0^{\circ}$  C. were added; on shaking, a clear solution resulted; it was allowed to remain quietly for twenty-four hours at the ordinary temperature; the monobromide had now risen to the surface of the hydrobromic acid as a light brown-colored layer. The cylinder was now vigorously shaken from time to time, to bring any

unaltered propylideneacetic acid which might be dissolved in the monobromide, into intimate contact with the hydrobromic acid. After this occasional shaking had been continued four or five days, the contents of the cylinder formed two distinct layers; the reaction was ended and all the propylideneacetic acid had been quantitatively changed into  $\beta$  bromvalerianic acid. The cylinder, still stoppered, was now placed in ice-water to cause the new acid to solidify, this, however, did not occur. It was then placed in a freezing mixture of ice and salt, and on agitating slightly, the monobromide at once congealed to a mass of fine needles lying on the surface of the hydrobromic acid. The cylinder stood for fifteen hours at a temperature of  $15^{\circ}\text{C}.$ ; then the crystalline cake was broken through with a glass rod, distributed through the hydrobromic acid, and brought into a platinum cone where it was allowed to dry, being washed with small successive portions of ice-water, in order to remove the greater part of the mineral acid. The contents of the cone were now brought upon a watch-glass and placed in a vacuum over sulphuric acid and potassium hydroxide; a dry sandy-white substance resulted, which was powdered and recrystallized out of petroleum ether. So produced, the  $\beta$  bromvalerianic acid is, after drying, perfectly pure, as the analysis proves.

0.233 gram of the substance dried in a vacuum gave 0.2410 gram AgBr.

Calculated for  $\text{C}_5\text{H}_7\text{BrO}_2$ .

44.20 per cent. Br.

Found.

44.20 per cent. Br.

$\beta$  bromvalerianic acid melts at  $59^{\circ}$  to  $60^{\circ}\text{C}.$ , the melting-point not altering in the least by repeated determinations on the same sample.

It dissolves readily in ether, chloroform, carbon disulphide, less easily in benzene and petroleum ether, and is almost insoluble in water of  $0^{\circ}\text{C}.$

If the cold, saturated solution of the monobromide in petroleum ether be allowed to evaporate spontaneously it crystallizes out in beautiful, colorless, eight-sided prisms.

The crystals set up after Naumann's system give the following crystallographic measurements:

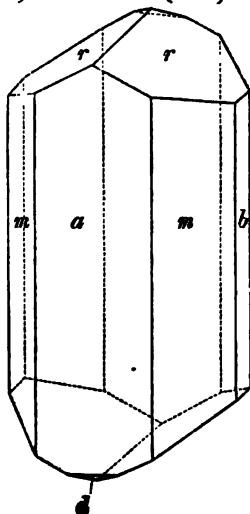
$\beta$  BROMVALERIANIC ACID.

Crystal system : Monosymmetric.

$$a : b : c = 1.4688 : 1 : 0.4900$$

$$\beta = 79^{\circ} 58' 45''$$

Observed forms:  $m = \{110\} \infty P$ ,  $a = \{100\} \infty \bar{P}\infty$ ,  $b = \{010\} \infty \bar{P}\infty$ ,  
 $r = \{011\} P\infty$ ,  $d = \{\bar{1}01\} + \bar{P}\infty$ ,  $e = \{101\} - P\infty$ .



The crystals are mostly two to five mm. long by one to two mm. wide, and possess a valerianic acid-like odor.

Some crystals are minus  $[\bar{1}01] + \bar{P}\infty$ , as also  $[100] \infty \bar{P}\infty$ , while  $[10\bar{1}] - \bar{P}\infty$  was only observed once.

The faces were almost always smooth and polished, giving excellent reflexes.

The following angles were measured and calculated:

	Measured.	Calculated.
$r : r = (011) : (0\bar{1}1) =$	$51^{\circ} 31'$	.....
$a : m = (100) : (110) =$	$55^{\circ} 20' 30''$	.....
$r : m = (011) : (\bar{1}00) =$	$99^{\circ} 1'$	.....
$m : m = (110) : (1\bar{1}0) =$	$110^{\circ} 43'$	$110^{\circ} 41'$
$m : b = (110) : (010) =$	$34^{\circ} 47'$	$34^{\circ} 39' 30''$
$r : b = (011) : (010) =$	$64^{\circ} 6'$	$64^{\circ} 14' 30''$
$a : b = (100) : (010) =$	$89^{\circ} 58'$	$90^{\circ}$
$a : d = (100) : (\bar{1}01) =$	$99^{\circ} 2'$	$99^{\circ} 12'$

	Measured.	Calculated.
$r : m = (011) : (\bar{1}\bar{1}0) =$	$74^{\circ} 2'$	$74^{\circ} 26'$
$a : e = (100) : (101) =$	$61^{\circ} 59'$	$62^{\circ} 44'$
$r : d = (101) : (\bar{1}01) =$	$36^{\circ} 33'$	$36^{\circ} 29'$
$r : m = (011) : (110) =$	$63^{\circ} 33'$	$63^{\circ} 28'$
$r : d = (011) : (\bar{1}01) =$	$31^{\circ} 8'$	$31^{\circ} 45'$
$d : m = (\bar{1}01) : (\bar{1}00) =$	$80^{\circ} 11'$	$80^{\circ} 48'$

A cleavage could not be found. The plane of the optical axes stands at right angles to the klinopinacoid and is only slightly inclined towards the orthopinacoid.

Obtuse bisectrix =  $\bar{b}$  axis.

$\beta$  Oxyvalerianic acid,  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—CH}_2\text{—COOH}$ .

The acid mixture from the treatment of ethylidenepropionic with caustic soda was not completely volatile with steam.

The residue left in the distillation flask, after the ethylidenepropionic and propylideneacetic acid had been driven over, had a strong acid reaction and gave up a yellow oil when shaken with ether. It was purified by dissolving in ether and precipitating with petroleum ether as a thick colorless liquid. This syrup could not be solidified either by allowing it to remain in a desiccator or at a temperature of  $18^{\circ}\text{C}$ . for several hours, aided by frequent stirring with a platinum wire. A portion of the acid, which had been prepared from the perfectly pure barium salt, was dried in a desiccator to constant weight; it then presented an absolutely colorless liquid, which, when put into a narrow test-tube and placed in a freezing mixture, would not become solid with frequent stirring by means of a platinum wire. At best it remained a colorless molasses-like liquid, although the barium salt from which it was obtained as well as the acid itself, as far as purity is concerned, left nothing to be desired as the analyses show.

0.2745 gram obtained from the pure barium salt contained in a platinum boat and dried in a desiccator gave 0.2073 gram  $\text{H}_2\text{O} + 0.5105$  gram  $\text{CO}_2$ .

	Calculated for $\text{C}_4\text{H}_8\text{O}_3$ .	Found.
C .....	50.85 per cent.	50.72 per cent.
H.....	8.47     "	8.39     "

$\beta$  oxyvalerianic acid is easily soluble in cold water, ether, benzene, and in chloroform; in carbon disulphide and petroleum ether it is insoluble.

From forty-five grams of ethylidenepropionic acid, which was boiled with caustic soda, 16.5 grams or thirty-six per cent. of  $\beta$  oxyvalerianic acid was produced.

*Salts of  $\beta$  Oxyvalerianic Acid.*—Calcium Salt. The still yellow-colored acid was diluted with water and heated on the water-bath until the mixture reacted neutral; it was then filtered and the yellow-colored filtrate decolorized with animal charcoal; the filtered solution was now evaporated until a pellicle formed on the surface and was then allowed to cool; the pellicle was dissolved and after remaining at the ordinary temperature for some time there was deposited on the bottom of the vessel a collection of white opaque warts of porcelain-like appearance, which, when powdered and dried in the air, was analyzed.

- |   |                 |
|---|-----------------|
| 1. 0.43 gram of air-dried salt lost 0.0263 gram $H_2O$ at $175^\circ C$ . |                 |
| Calculated for $(C_5H_7O_3)_2, Ca + H_2O$ .                               | Found.          |
| 6.16 per cent. $H_2O$ .   | 6.12 per cent.  |
| 2. 0.1889 gram anhydrous salt gave 0.0915 gram $CaSO_4$ .                 |                 |
| Calculated for $(C_5H_7O_3)_2, Ca$ .                                      | Found.          |
| 14.59 per cent. $Ca$ .  | 14.30 per cent. |

The salt retains its water of crystallization very tenaciously and gives it up when heated for some time at  $175^\circ C$ . At  $180^\circ C$ . it begins to melt and acquire a yellow tint, whereby it loses considerable in weight and at  $200^\circ C$ . a yellow transparent molten mass filled with bubbles results, with an increase in the amount of decomposition, which began at  $180^\circ C$ . The salt is quite soluble in water and insoluble in alcohol. Still the aqueous solution, to which three volumes of absolute alcohol has been added, remains perfectly clear at first, only becoming cloudy after the lapse of some hours, and after a longer period the salt is deposited as a sandy indistinctly crystalline mass.

Treated with alcohol on a slide and examined under the microscope the following was observed:

The precipitate consists of small, mostly irregularly formed, double refracting leaves, stretched at times in one direction, and which present an oblique obliteration of light, parallel to this principal direction of development. Because of this oblique obliteration the crystals probably belong to the monoclinic system.

*Barium Salt.*—The barium salt was prepared in exactly the same manner as the preceding, by warm neutralization of



barium carbonate; the solution evaporated to a pellicle, was allowed to cool, the pellicle not dissolving; after about an hour it became cloudy, and deposited small, fine needles, which gradually accumulated on the bottom of the beaker as a sandy crystalline mass.

This crystalline mass treated with alcohol and examined under the microscope, showed a colorless, strongly double refracting homogeneous number of crystals, grouped to a half ball; they were tables of rhombic or right angular form, with an oblique obliteration and were, therefore, probably monoclinic.

0.1983 gram of the air-dried salt lost 0.0093 gram  $H_2O$  at  $105^\circ C.$  and gave 0.1193 gram  $BaSO_4$ .

	Calculated for $(C_3H_5O_2)_2, Ba+H_2O.$	Found.
$H_2O$ .....	4.63 per cent.	4.67 per cent.
Ba .....	35.22    "	35.36    "

At  $105^\circ C.$  the salt melts without decomposition to a colorless transparent mass; even, on the water-bath, when covered with a little water a thick syrup results. It is insoluble in alcohol.

**Silver Salt.**—The silver salt was obtained by the double decomposition of a warm concentrated solution of the calcium salt with silver nitrate, as slightly violet-colored crystals or a powder according as it separated out rapidly or slowly. When recrystallized from hot water it is nearly white and is but little affected by light.

0.1037 gram of the salt dried at  $50^\circ$  to  $55^\circ C.$  gave in the combustion 0.0497 gram Ag.; 0.1018 gram  $CO_2$ ; and 0.0390 gram  $H_2O$ .

	Calculated for $(C_3H_5O_2)_2 Ag.$	Found.
Ag. ....	48.00 per cent.	47.93 per cent.
C .....	26.67    "	26.86    "
H.....	4.00    "	4.27    "

Microscopically the crystalline powder appeared to be fine, flat, at times, corroded needles, which had an oblique obliteration in their long direction.

**Boiling  $\beta$  Oxyvalerianic Acid with Sodium Hydroxide.**—For this very interesting experiment 6.240 grams of calcium  $\beta$  oxyvalerianate (representing five grams of acid) was used; through double decomposition with sodium carbonate sodium  $\beta$  oxyvalerianate was formed and this boiled for thirty hours in a copper flask connected with a return condenser and containing 17.1 grams, of sodium hydroxide in 154 grams of water.

After cooling, the solution was acidified with sulphuric acid and extracted with ether. The ethereal residue rapidly boiled with water and a few drops of dilute sulphuric acid, to change any  $\gamma$  oxy acid present (which could have originated from the  $\beta$  oxy acid with ethylidenepropionic acid and valerolactone as intermediate steps) into lactone, was then made slightly alkaline with sodium carbonate, and shaken out with ether; nothing was taken up by the latter, consequently, the presence of  $\gamma$  oxy acid must be excluded.

The alkaline solution, after the ether had been removed, was acidulated with sulphuric acid and distilled with steam until the distillate passed over the neutral. The unaltered  $\beta$  oxy acid remained behind in the distillation flask, which, when shaken with ether, allowed of its removal from the contents of the same; it was converted into the calcium salt, which amounted to three and four-tenths grams or more than one-half of the acid originally employed.

The acid distillate was neutralized with barium carbonate, but since the barium salts thus obtained do not allow a good separation with alcohol, they were converted into the sodium salts through the aid of sodium sulphate, and now the  $\beta \gamma$  acid converted into lactone by boiling with sulphuric acid, made alkaline with soda solution, the lactone was shaken out with ether, and characterized by boiling with barium hydroxide for thirty minutes, thus converting it into the barium salt of  $\gamma$  oxyvalerianic acid. After precipitating the excess of barium with carbon dioxide in the heat, the evaporated filtrate gave 1.973 grams of an amorphous substance easily soluble in alcohol and water, from which it was deposited as a gummy mass, and proved in all its conduct to be the barium salt of  $\gamma$  oxy acid. Finally by exactly precipitating with sulphuric acid in the heat, and adding potassium carbonate to the cold filtrate in a narrow tube the valerolactone was obtained as a supernatant layer.

The alkaline solution freed from lactone was acidulated with sulphuric acid and distilled with steam; from the acid distillate through neutralization with calcium carbonate 0.94 gram of calcium propylideneacetate was obtained, from which the acid itself was freed. After purifying in the manner already mentioned it melted at  $7\frac{1}{4}^{\circ}$  to  $8\frac{1}{4}^{\circ}$  C.

In the process of boiling with caustic soda, there was obtained from the  $\beta$  oxy valerianic acid :

56.6 per cent. of unaltered oxy acid.

21.26 per cent. of ethylidenepropionic acid.

14.64 per cent. of propylideneacetic,

with a loss of 6.5 per cent.

*Distillation of the  $\beta$  Oxyvalerianic Acid.*—A portion of the thick, almost colorless, acid was so distilled from a small distillation flask that it passed over slowly and in drops. As the boiling began, the thermometer with its bulb in the liquid indicated  $190^{\circ}\text{C}.$ ; it was now raised until its bulb was just beneath the exit tube; it sank to  $180^{\circ}\text{C}.$ , but rapidly rose to  $190^{\circ}\text{C}.$ , where it remained constant for a short time, gradually rising to  $195^{\circ}\text{C}.$ , and then to  $200^{\circ}\text{C}.$ , where the principal portion went over, and finally to  $203^{\circ}\text{C}.$ ; the last drops of the distillate were colored yellow, and a small tarry residue only remained in the flask. The distillate, which had the same empyreumatic odor as that from methylparaconic acid, was mixed with five times its volume of water and sufficient sodium carbonate to render it distinctly alkaline after a vigorous shaking; nothing could be extracted by means of the ether, consequently, the distillate contained no lactone and a conversion of  $\beta$  oxyvalerianic acid into  $\gamma$  oxy acid respectively  $\gamma$  lactone had not taken place. The salt solution, free from ether, was now acidulated and distilled with steam, in order to separate the unsaturated acids from the oxy acid. The milky distillate was neutralized with barium carbonate and thereby the mixed barium salts of the volatile acids obtained; as, however, these can not be satisfactorily separated with alcohol, the above-described process used to effect their separation when produced by boiling the oxy acid with caustic soda was employed and the  $\beta$   $\gamma$  acid separated as lactone from the  $\alpha$   $\beta$  acid; the latter was characterized by means of its melting-point.

From the residue of the distillation with steam a small amount of the  $\beta$  oxy acid could be extracted.

The principal product in the distillation of the  $\beta$  oxyvalerianic acid was propylideneacetic acid; only a small quantity of ethylidenepropionic was found, and a like small portion of oxy acid went over unaltered.

The three isomers allylactic, ethylidenepropionic, and pro-

pylideneacetic acids, can, as the accompanying table shows, be easily characterized and distinguished.

But recently Fittig and Mackenzie<sup>1</sup> have for the sake of simplicity, applied the terms  $\gamma$   $\delta$ ,  $\beta$   $\gamma$ , and  $\alpha$   $\beta$  pentinic acids to the allylacetic, ethylidenepropionic, and propylideneacetic acids, respectively.

	Allylacetic acid.	Ethylidenepropionic acid.	Propylideneacetic acid.
Free acid.	Fluid, boiling-point 186°-187° C., characteristic odor resembling that of valerianic acid.	Fluid, boiling-point 193°-194° C.	Solid melts at 74-84° C.
Calcium salt.	Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms, which are insoluble in alcohol.		Crystallizes out of the aqueous solution in the cold, with four molecules of water of crystallization Soluble in hot absolute alcohol.
Barium salt.	Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms. Insoluble in alcohol.		Crystallizes in the cold out of the aqueous solution with two and four molecules of water. Soluble in hot absolute alcohol.
Monobromide.	Both acids produce the same $\gamma$ bromvalerianic acid with hydrobromic acid. Fluid and not solid at -16° C.		<p>Gives with hydrobromic acid <math>\beta</math> bromvalerianic acid. This crystallizes out of petroleum ether in monoclinic prisms with the following forms:</p> <p><math>\infty P_{20} \infty P_{\infty} P_{20} P_{\infty} + P_{\infty} - P_{\infty}</math>, melts at 59°-60° C.</p> <p>Insoluble in water, becomes liquid in water of 45°-50° C.</p>
Dibromide.	Thin four-sided monoclinic tables melting at 58°. Difficultly soluble in petroleum ether.	Monoclinic prisms developed in the direction of the C axis. Readily soluble in warm petroleum ether; less so in cold. Melting-point 65°; dissolves in water with a gyratory motion. Becomes fluid under water of 50°-55° C.	Monoclinic prisms melting at 56°, becoming liquid under water of 15° C. Very readily soluble in petroleum ether at the ordinary temperature.

WESTERN RESERVE UNIVERSITY,  
MEDICAL DEPARTMENT,  
CLEVELAND, OHIO.

<sup>1</sup> Dissertation, Strassburg, 1894.

## THE PHOSPHOMOLYBDIC ACID TEST AS APPLIED TO LARD ANALYSIS.

BY GEORGE F. TENNILLE.

Received November 5, 1894.

THE phosphomolybdic acid test has been of late so strongly recommended for use in the detection of cottonseed-oil in lard that it seemed to the writer that the record of the results of a rather thorough trial of this reagent would be of interest to chemists.

The test was originally proposed by P. Welmans in the *Pharm. Zeit.*, 1891, 36, 798. One gram of the oil or fat was dissolved in five cc. of chloroform, two cc. of phosphomolybdic acid solution were added, and the mixture shaken. On standing, the liquid separated into two layers, the lower of which was colorless and the upper of which had become green, if any vegetable oil were present. The addition of an alkali changed the green to a blue color. Lard, tallow, goose fat, and butter fat were said not to show any green coloration, and the only animal oil which gave the test was cod-liver oil.

It was supposed that at last the reagent had been discovered which would serve to detect any addition of cottonseed or other vegetable oils to lard, no such one test having previously been satisfactory. Very shortly this reaction was recommended for such a use by a number of chemists. Among others, Engler and Rupp, Wimmer, Mansfeld, and Goske approved of its efficacy. H. Schweitzer and E. Lungwitz (*J. Soc. Chem. Ind.*, June, 1894, 614) state that they have found the reagent of great use.

Wallenstein, the first to criticise the test, (*J. Soc. Chem. Ind.*, 1893, 55) states that tallow gives a green coloration when tested with the phosphomolybdic solution. To satisfy myself in regard to this point raised by Wallenstein I have tested a large number of samples of tallow, and other qualities of beef fat—such as might be used in adulterating lard or in the manufacture of compound lard—and have in no case obtained a green color.

J. Lewkowitsch (*J. Soc. Chem. Ind.*, June, 1894, 617) has made an extended series of experiments with different fats and

oils in regard to the colors given with phosphomolybdic acid. He writes in part as follows: "Of all the samples only lard had remained colorless and there seemed to be ground for the opinion that cottonseed-oil or any other seed-oil employed for adulteration might easily be detected by phosphomolybdic acid. I prepared, therefore, a number of mixtures of pure, freshly rendered lard, yielding no coloration with Welman's test and of cottonseed-oil giving a distinct blue reaction." In testing these mixtures, he found that up to those containing thirty-five per cent. of cottonseed-oil the color of the upper layer was yellow, and at thirty-five per cent., on making this test alkaline, he only obtained a faint blue coloration. He continues: "This table clearly demonstrates the necessity of using Welman's test with great caution. In practical analysis an adulteration of ten per cent. cottonseed-oil would escape detection if freshly rendered lard had been used. Indeed, pure lard mixed with fifteen per cent. cottonseed-oil gave reactions just like sample number sixty-three in the preceding table." (Sample number sixty-three was a lard slightly rancid, six years old and gave a test remaining yellow when acid, and only faintly blue when alkaline.) "Welman's reaction can therefore be admitted only as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a given sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Of course it is understood that the original color of the phosphomolybdic acid solution is a decided yellow. The green color produced by a certain sample is not of as deep a shade as the corresponding blue color when the acid has been neutralized by ammonia. Hence a light green tinge, which would be difficult to observe on account of the initial yellow color of the reagent, would be most readily seen when changed to a blue by the alkali.

Of all the samples of cottonseed-oil, which I have tested, each one gave a green color, though I find that the color varies much in depth with different oils. It seems to be a general rule that the more refined the oil the less heavy the coloration. Thus a crude oil will color intensely green, a yellow oil perhaps less so,

and a white oil still less. The age of the oil and the method of refining also in a great measure modify the color. In his tests on percentages, J. Lewkowitsch states that he used in making the mixtures a cottonseed-oil which gave a distinct blue reaction. The oil probably did not, therefore, show a deep green coloration and the test on the oil had to be made alkaline to produce a color which was decided. He must have used, I should judge, either an unusual oil or a weak solution of the reagent. For such oils as would commonly be employed for adulterations or compounding I think that ten to fifteen per cent. in a mixture would show a decided green coloration.

Samelson (*Ztschr. anal. Chem.*, 1894, 189) comes to the conclusion that the phosphomolybdic acid test is of no value and that the iodine-absorption figure is the only reliable test for the detection of cottonseed-oil in lard. He states that six samples of American lard are undoubtedly impure because they have Hübl figures of from 64.7 to 67.2, which are higher than any figures hitherto recorded by scientific investigators for pure hog fat. On this assumption hangs the result of his investigation of Welman's test.

I have often tested lards of undoubted purity for their iodine-absorption figures and obtained results as high as from 62.7 to 66.4. On the other hand, as will be seen later, the Hübl figures for pure lard can run as low as 47.7. It must be remembered that lards are sold in large amounts in the American market which do not represent the whole fat of the hog, but simply a portion. It is a well-known fact that fats from different parts of the hog vary greatly in their iodine figures, hence, lards made from different portions of the fat would also vary. Wiley (U. S. Dept. Ag. Bul., 13, Lard and Lard Adulterations, 1889), states in order to show the great difference in the absorption power for iodine of the different fats of the hog, as follows, "For instance, a sample of intestine lard absorbed 57.34 per cent. of iodine; the leaf lard from the same animal absorbed 52.53 per cent.; the foot lard 77.28 per cent.; the head lard 85.03 per cent. In the prime steam lards mentioned the percentage of iodine absorbed was from 60.34 to 66.47 per cent., and the mean 62.86 per cent." The iodine test alone would certainly not be of much service for

the detection of vegetable oils in lard, when the iodine figure of the lard itself may vary as I have found, from 44.70 to 66.40. As may be calculated, thirty per cent. or more of cottonseed-oil could be added to a lard with an iodine figure of 44.7 without the iodine figure of the mixture reaching beyond the figures of pure lard. Hence it will be seen, I think, that the condemnation of a lard as adulterated with cottonseed-oil on the ground of a high iodine figure would be hasty and might easily be erroneous.

In the literature, then, of this test up to the present time, the preponderance of the writing is in its favor, and only two legitimate limitations are placed upon its accuracy, one, that tallow might give the same results as cottonseed-oil, and the other, that a certain comparatively small percentage of cottonseed-oil might escape detection. At first blush, one would think, therefore, that the test would be of value in preliminary examinations of samples suspected of sophistication; namely, that a negative test would show the lard contained not more than ten per cent. of cottonseed-oil, and, as the addition of less than ten per cent. would hardly pay the renderer, was, therefore, probably free from vegetable oils, and that a positive test would almost conclusively point to the presence of a vegetable adulterant.

After the careful examination of a great number of lards I have come to the conclusion that a positive test does not prove the presence of such an adulteration.

In my investigation the test has been carried out as follows:

About one gram of the melted fat is placed in a test-tube and dissolved in five cc. of pure chloroform, two cc. of a ten per cent. solution of phosphomolybdic acid are then added and the test-tube vigorously shaken. After standing, and the mixture having separated into two layers, the color of the upper liquid is observed by comparison with a test run in exactly the same manner on a sample of pure laboratory rendered lard. I do not consider a test as decisive unless a very apparent green tinge appears, relying more upon the green coloration than upon the slight blue shades produced after making doubtful greenish-colored tests alkaline with ammonia.

The lards upon which most of my tests were made were of



those grades known in New York City as No. 1 lard, Prime City lard, and Prime Western lard. A brief account of the manner in which these lards are rendered and their difference in fat composition may be of help to the better understanding of their often dissimilar chemical properties. These three grades of lard make up the bulk of the lard sold to the refiners in the vicinity of New York City.

No. 1 lard generally sells at a trifle lower figure than Prime City lard, say as a limit, half a cent per pound, though often it commands the same price. It is a harder fat than City or Western and is all steam-rendered. In color it often has a distinct green tinge and will generally carry a higher steam flavor. It is rendered by the slaughterers and is made up of gut fat with once in a while a little trimmings. No leaf lard is in it as the leaf is sold with the carcass to the butchers. After slaughtering, the fat is stripped from the still warm intestines and carefully washed and goes together with a certain proportion of trimmings to the rendering kettle, where it is subjected to steam under pressure. When the process is complete the water, etc., is drained off and the lard placed in tierces for sale. This lard is made in and about New York City, the hogs being brought from the West and slaughtered here.

Prime City lard is made by the butchers and may be either rendered in open kettles with free fire or steam-rendered in the same manner as No. 1 lard. This lard sells as a usual thing one-half cent per pound below Prime Western lard. The kettle-rendered is darker in color than the steam lard and has a characteristic taste and smell.

City lard is made of the trimmings, head fat, foot fat, backbone fat (perhaps some back fat), and any leaf which can not be sold over the counter, which fats accumulate in large amounts in the butcher shops. There is seldom any leaf lard in it as the leaf can be sold more profitably at retail for domestic rendering. The lard is usually a trifle softer than Western lard and not as good in color or flavor though better in these respects often than the No. 1 lard.

Prime Western lard is steam-rendered, of good color, high steam flavor, and a harder fat than City, but less so than No. 1.

It is rendered by the large slaughtering houses of the West in immense quantities and consists of gut fat and sometimes a little trimming.

Head fat often goes into this lard and the leaf at times may be a constituent. But only when the leaf can not be sold in the form of "neutral" lard for butterine does leaf lard find itself in the Western lard. Some back-bone fat at times may be present. The lard is shipped to the East in tierces and tank cars.

The first sample of No. 1 lard tested gave a decided green color. After further analysis the absence of any vegetable adulteration was pretty conclusively proven, and thinking that this might be a sporadic case only, samples of this grade of lard were obtained from all the firms who were rendering it in the vicinity of New York. On testing, each sample gave an undoubted green coloration, some, however, being more decided than others. After further examination of the lards it was decided that they

	Häbl figure.	Titre ° C.	Rise of temperature with sulphuric acid, ° C.	Bechi's silver nitrate test.	Millian's silver nitrate test.	Welman's phosphomolybdic acid test.	Microscope.	Free fatty acid. Per cent.	Specific gravity, 98° C. 15° C.
1.	54.5	41.4	30.5°	Negative.	Slight discoloration.	Decided green. Blue if alkaline.	Lard only.	...	.....
2.	55.6	41.4	31.8°	"	"	"	"	...	.....
3.	58.6	40.2	34.8°	"	"	"	"	...	.....
4.	53.7	41.4	30.0°	"	"	"	"	0.73	0.8595
5.	55.4	41.4	31.5°	slight discoloration.	"	"	"	...	.....
6.	56.1	41.4	31.7°	negative.	"	"	"	...	.....
7.	47.7	42.4	25.5°	slight discoloration.	"	"	"	...	.....
8.	51.7	41.8	31.5°	negative.	"	"	slight indication of beef.	...	.....
9.	52.0	41.9	29.5°	slight discoloration.	"	"	"	...	.....
10.	48.9	...	...	.....	.....	"	.....	...	.....

were pure hog fat. To corroborate the results a sample of the stock from which the lard is rendered was procured and after cleansing, was rendered in the laboratory. The resulting lard gave a decided green coloration with phosphomolybdic acid. The tests made upon nine samples of No. 1 lard and one sample of lard rendered in the laboratory from No. 1 lard stock may be seen in the table. Lards 1 to 9, inclusive, are those obtained

from the renderers. Lard 10 is that rendered in the laboratory.

The iodine-absorption figure was obtained in the usual manner, great care being taken in the manipulation, duplicates being run, blanks carried through with each test, and the flasks in which the determinations were made being furnished with ground-glass stoppers and gutters to hold a solution of potassium iodide seal, to prevent as far as possible any loss of iodine in vapor.

The "titre" is the crystallization temperature of the separated, washed, dried, and filtered fatty acids. The highest point which the mercury reaches, after the rise of temperature due to the liberation of the latent heat has begun, is the temperature recorded.

The rise of temperature with sulphuric acid is of no absolute value as each chemist has his own method of manipulation. The results of the test are simply given for comparison with each other in connection with the corresponding Hübl and "Titre" figures.

The Bechi test was carried out upon the glycerides using an alcoholic solution of silver nitrate. The words "slight discoloration" do not indicate the presence of cottonseed-oil which, in appreciable amounts, produces heavy blackening and often a silver mirror.

The Milliau modification of the Bechi silver nitrate test was carried out upon the fatty acids and the discoloration produced in each case was of a very slight character.

Welman's phosphomolybdic acid test on each sample showed a decided green color and on saturation of the mixture with ammonia the test turned a decided blue. By the words "decided green," in the table is meant, not a greenish yellow tinge, but a green color that was unmistakable to the eye. On the other hand, the tests were not of that deep emerald shade, such as a large percentage of cottonseed-oil would exhibit.

The microscopical examination was carried out upon crystals formed from saturated solutions of the fats in ether and showed in but one case any suspicion of the presence of beef fat, and here, sample 8, the result was doubtful.

The free fatty acid percentage was obtained in the usual way by titration and the use of phenolphthalein as indicator. The result was calculated to oleic acid.

The specific gravity was taken with a Westphal balance, the fat at a temperature of 98° C. being compared with an equal volume of water at 15° C. No correction was made for the expansion of the glass of the bob.

These lards were all hard fats with generally a high steam flavor, but with an inferior color.

It will be seen that there is quite a variation in the Hübl figures of the lards in the table; *viz.*, from 47.7 to 58.6. This is explained on glancing through the next column, when one notices that the titre decreases with approximately the same regularity with which the Hübl increases. The titre is a good guide to the hardness of the fat, that is, to the proportion of liquid to solid glycerides. As the amount of oleic glyceride increases in proportion to the amounts of stearic and palmitic glycerides, the fat becomes softer, the titre test is lower, and consequently, owing to the greater preponderance of unsaturated glyceride, the iodine-absorption figure becomes higher. The lards then owe their difference in Hübl figures to the difference in their fat composition. In the different rendering establishments, the proportion of fats used from different parts of the hog evidently varied. I consider that all the samples consisted of pure hog fat without any cottonseed or other vegetable adulteration. What constituent of this class of lards it is that has the reducing action upon the phosphomolybdic acid, I do not pretend to say. Whether it is a normal product of that portion of the fat of the hog, or simply an impurity introduced or not eliminated in the rendering process, or a peculiarity imparted to the fat at certain seasons of the year, or due to feeding, I am undecided.

Nearly all of the many samples of City lard, both steam and kettle-rendered, tested gave a negative result. In one or two cases, slight green tinges were observed. Of the fifty-seven undoubtedly pure samples tested, each representing on an average 100 tierces of lard, fifty gave no green color and seven gave a slight green tinge.

Western steam lard often gives a slight green test. Of the twenty-nine undoubtedly pure samples tested, each representing on an average 100 tierces, nineteen gave no green and ten a

slight green color. The tests were not as decided as those on the No. 1 lard but still distinctly visible. These results are probably due to the presence of the large percentage of No. 1 lard which the Western lard contains.

I might say further that lard rendered from the leaf alone, which does not, as far as I know, find its way to the lard market in this country, does not give a green color with the reagent. This fact may have been the cause of the many favorable endorsements which appeared after the first publication of the reaction. In order for the chemist to make a fair trial of the reagent, what, apparently, would appear fairer than to obtain a leaf and render it in the laboratory and make tests upon this lard?

In conclusion, I would say, that for the detection of less than ten to fifteen per cent. of cottonseed-oil the test is unreliable, as, in such an instance, no reaction may be produced. When a slight green is the result of a test, the presence of cottonseed-oil is not proven. When a heavy green color, deep emerald in shade, is obtained, the addition of a vegetable oil in considerable amounts is fairly certain. But it is easy to detect such large additions by other methods, and the phosphomolybdic test may be considered to be of slight analytical value and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cottonseed or other vegetable oils in lards.

LABORATORY OF THE CENTRAL LARD COMPANY,  
October 29, 1894.

## SOME NEW SOLVENTS FOR PERCHROMIC ACID.<sup>1</sup>

BY WILLIAM M. GROSVENOR, JR.

Received November 8, 1894.

ON the addition of hydrogen peroxide to an aqueous solution of potassium dichromate acidified with sulphuric acid, a blue color is produced, which is supposed to be caused by the formation of perchromic acid. Ether dissolves the blue substance, forming an intensely colored, deep blue solution. On standing, the perchromic acid in this solution decomposes with the formation of chromic acid or salts of chromium.

Recently, Griggi (*J. Chem. Soc.*, 64, 2,223) has stated that

<sup>1</sup>Read before the New York Section, December 8, 1893.

perchromic acid is also soluble in amyl alcohol, and that this solution is more stable than the ethereal solution, the color lasting for six hours. With a view to studying the behavior of perchromic acid toward certain substances, various organic liquids were tried as solvents for perchromic acid. A two per cent. solution of potassium dichromate was slightly acidified with sulphuric acid and then shaken with the solvent and hydrogen peroxide, after which it was allowed to stand. The following substances failed to dissolve the perchromic acid:

Carbon disulphide, benzene, ligroin, spirits of turpentine, castor oil, oil of wintergreen, oil of bergamot, kerosene, paraffin oils, chloroform, carbon tetrachloride, toluene, nitrobenzene, and aniline.

The following substances were found to be solvents for perchromic acid:

Ethyl acetic ester, valerianic ether, amyl valerianic ester, amyl chloride, amyl butyric ester, amyl formic ester, and amyl acetic ester.

In order to determine which of the solutions of perchromic acid lasted the longest, the following experiments were made. Equal amounts of a dilute solution of chromic acid were shaken in the presence of the solvents with equal amounts of hydrogen peroxide, in small oil-sample bottles, and allowed to stand on a window frame exposed to a strong light. The temperature varied from  $10^{\circ}$ – $20^{\circ}$  C. The results were as follows:

Amyl alcohol retained its color one hour and ten minutes, then turned brown.

Amyl chloride retained its color one hour and fifty-five minutes, then turned colorless.

Amyl butyric ester retained its color one hour and fifty-five minutes, then turned brown.

Amyl valerianic ester retained its color two hours and ten minutes, then turned green.

Valerianic ether retained its color two hours and thirty-five minutes, then turned colorless.

Amyl formic ester retained its color sixteen hours and fifty-five minutes, then turned white.

Amyl acetic ester retained its color seventeen hours and fifty-five minutes, then turned colorless.

Ethyl ether retained its color eighteen hours and twenty-five minutes, then turned colorless.

Ethyl acetic ester retained its color twenty-three hours, then turned colorless.

These results do not agree with the observations of Griggi, that the amyl alcohol solution of perchromic acid is more stable than the solution in ether. The most stable solution is that in ethyl acetic ester. The time of duration given by Griggi, six hours, was evidently found under different circumstances. If the layer of the solvent is allowed to remain upon the aqueous layer the decomposition of the perchromic acid is greatly accelerated. The above experiments were made in this manner. Those of Griggi may, perhaps, have been made under other conditions in this respect.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

### SOME FACTS OBSERVED IN THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDIC ACID PROCESS.

BY RUDOLF DE ROODE.  
Received November 24, 1894.

THE length of time necessary for the complete precipitation of phosphoric acid seems to be much less than is generally supposed. Portions of the same solution were treated with molybdic solution and allowed to stand at 65° C. for five, ten, fifteen, twenty, thirty, forty, fifty, and sixty minutes, respectively, and two portions stood in a warm place over night. The phosphoric acid determined as usual as magnesium pyrophosphate, showed that the precipitation was complete after standing only five minutes. The weights of magnesium pyrophosphate were as follows:

5 minutes.....	0.0676 gram	} Average 0.0673
10    "       .....	0.0672   "	
15    "       .....	0.0674   "	
20    "       .....	0.0672   "	
30    "       .....	0.0669   "	
40    "       .....	0.0670   "	
50    "       .....	0.0673   "	
60    "       .....	0.0675   "	
12 hours.....	0.0671   "	
24    "       .....	0.0676   "	

By making a determination of phosphoric acid, using twenty-

five cc. of a very dilute sodium phosphate solution and the same quantities of reagents as are used in a regular determination, and then adding twenty-five cc. of this same dilute sodium phosphate solution to a regular determination and using the first determination as a blank which is subtracted from the last, we get a lower result, which would seem to indicate that a regular determination, without the addition of the phosphate solution and subtraction of the blank, gives too high a result.

A dilute sodium phosphate solution (twenty-five cc.) gave, with the same quantities of reagents as ordinarily used,

1.....	0.0158	gram of magnesium pyrophosphate.		
2.....	0.0161	"	"	"
3.....	0.0156	"	"	"
4.....	0.0163	"	"	"
5.....	0.0160	"	"	"
Average....	0.0160	"	"	"

Twenty-five cc. of an acid phosphate solution, together with twenty-five cc. of the above sodium phosphate solution and the same quantities of reagents gave

	0.0821	gram of magnesium pyrophosphate.		
Blank.....	0.0160	"	"	"
Difference....	0.0661	"	"	"

The average of the ten results obtained where no blank was subtracted was 0.0673 gram magnesium pyrophosphate, making a difference of 0.0012 gram.

Three of the weighed precipitates of magnesium pyrophosphate, in the series of ten, were redissolved in nitric acid, and reprecipitated with molybdic solution and magnesia mixture, ignited in the same crucibles and weighed. At first the magnesium pyrophosphate weighed :

1 .....	0.0672
2 .....	0.0670
3 .....	0.0671

After solution and reprecipitation :

1 .....	0.0660
2 .....	0.0660....
3 .....	0.0659



Again dissolved and reprecipitated as before :

1 .....	0.0659
2 .....	0.0658
3 .....	0.0657

There seems to be no further loss on reprecipitation, and the results, after the second and third precipitation, agree closely with the results obtained by using and subtracting a blank. These results also would indicate that somewhat too high results are obtained by the regular method for phosphoric acid determination.

Another fact along this same line was also observed ; *viz.*, that if different quantities of the same phosphate solution are precipitated, the larger quantity gives the lower and more correct result. Thus, twenty-five and fifty cc. of a phosphate solution, precipitated as usual, gave quantities of magnesium pyrophosphate which, when expressed in percentage of  $P_2O_5$ , were :

Twenty-five cc. gave 26.05 per cent. and 26.10 per cent.

Fifty cc. gave 25.96 per cent. and 25.97 per cent.

And another solution in like manner :

Twenty-five cc. gave 36.38 per cent.

Fifty cc. gave 36.18 per cent.

The most plausible explanation of this also seems to be that there is some source of error tending to give too high a result, which is multiplied more the smaller the quantity which is taken, and it would seem desirable, for the sake of accuracy, to employ as large a portion as is convenient.

The foregoing experiments seem to warrant the following conclusions :

1. That our present method for determining phosphoric acid seems to give results which are somewhat too high.

2. That the results obtained by using a large quantity of substance, and obtaining large precipitates, are lower and somewhat more accurate than those obtained where smaller quantities are employed.

3. That somewhat lower and more accurate results are obtained by using a blank made by employing a dilute solution of a phosphate, which is added to each determination. This blank, previously determined, being subtracted from the final result.

4. That accurate results, agreeing with those obtained by the

use of the blank, are obtained by redissolving the magnesium pyrophosphate and reprecipitating.

5. That five minutes digestion at 65° C. seems to be sufficient for the complete precipitation of phosphoric acid by molybdic solution.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
November 12, 1894.

### THE ADDITION OF CALCIUM CHLORIDE TO THE SOLUTION OF A FERTILIZER IN THE DETERMINATION OF POTASH.

BY RUDOLF DE ROODE.  
Received November 26, 1894.

MR. H. A. HUSTON has proposed the addition of a solution of calcium chloride to the solution of a fertilizer in the determination of potash, in order to furnish sufficient calcium to form tricalcium phosphate with all the phosphoric acid present, and thereby permit of the use of platinum dishes in the Lindo-Gladding method. In testing this proposition I find that when sufficient calcium chloride was added to combine with all the phosphoric acid present and then ammonia added in excess and a portion of the solution filtered off, no test for phosphoric acid could be obtained. But, that if in addition to the calcium chloride and ammonia, some ammonium oxalate or carbonate was added, a filtered portion of the solution *did* give a test for phosphoric acid. This is accounted for by the fact that the calcium phosphate, which was precipitated by the ammonia, is changed by the ammonium oxalate or carbonate into calcium oxalate or carbonate and ammonium phosphate, so that the very object for which the calcium chloride was added is defeated by the addition of the ammonium oxalate or carbonate. In order to make the use of calcium chloride effective it is necessary to filter off from the precipitate formed by the calcium chloride and ammonia and to then add the ammonium oxalate or carbonate to the filtrate. This necessitates two separate filtrations, and it is doubtful if we have in Mr. Huston's suggestion anything better than, or even so good as in the present alternate method.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
November 12, 1894.

## ON THE PREPARATION OF AMMONIUM CITRATE SOLUTION.

BY RUDOLF DE ROODE.

Received November 26, 1894.

**M**ANY times in preparing a solution of ammonium citrate, I have observed a fact which seems to indicate that the preparation of a strictly neutral solution is an extremely simple matter. If some citric acid is treated with ten per cent. ammonia until dissolved, the solution becomes quite hot, and if it is now diluted to nearly the proper specific gravity, made decidedly alkaline with ammonia, and allowed to stand over night in an open dish, it will be found in the morning to be strictly neutral.

Being warm and in an open dish the excess of ammonia escapes completely, leaving it neutral. For the last four or five times which I have had occasion to prepare an ammonium citrate solution, I have observed this fact and each time have found it unnecessary to alter the neutrality in the least degree. I find it very convenient. I also find it advantageous to add a small quantity of salicylic acid to the solution (about one gr. for five liters of solution is sufficient). This is added before neutralization, so that the salicylic acid is also neutralized by the ammonia. The salicylic acid prevents the growth of fungus in the solution and it remains unchanged a long time. Some solution six months old when used in fertilizer work, gave results practically identical with those obtained by the use of a freshly prepared solution.

AGRICULTURAL EXPERIMENT STATION,

MORGANTOWN, WEST VIRGINIA,

November 12, 1894.

## THE DETERMINATION OF POTASH IN MANURES.

BY W. E. GARRIGUES.

Received November 15, 1894.

**T**HE following method for the determination of potash in fertilizers, has been in use in the writer's laboratory for some months, and in view of its ease, quickness, and comparative accuracy is believed to be a decided improvement on that of Lindo-Gladding.

It depends upon: 1. The ignition of the material with sul-

phuric acid, thereby converting all potash present, to sulphate, if not already in that form, and at the same time expelling any ammonia and organic matter. 2. Precipitation of the sulphuric acid with barium chloride. 3. Precipitation of the excess of barium, together with other earthy bases, by sodium carbonate. 4. Evaporation of the filtrate with platinic chloride as usual.

The process entails but one filtration and evaporation and with due precaution the final precipitate of potassium platinochloride is obtained practically chemically pure.

The analysis: Ten grams of the sample are weighed into a platinum dish and worked into a paste with concentrated sulphuric acid. The rod is wiped with a small piece of filter paper, which is added to the sample, and the whole ignited, raising the heat gradually and finishing with a blast until the residue is white, or red if much iron be present.

The contents of the dish are now scraped out into a porcelain mortar and ground to a fine powder, a little hot water is added, washing out the dish at the same time, and the mass triturated for a few minutes. It is next washed into a 500 cc. flask and boiled with 250 cc. of water for half an hour, when a ten per cent. solution of barium chloride is run in five cc. at a time and boiling after each addition, until no further precipitation is visible.

Add a single drop of phenolphthalein solution and sodium carbonate, drop by drop, until a faint permanent rose color is obtained. Boil for a minute, set aside to cool, and make up to the mark. Filter through a dry paper and measure out fifty cc. of the filtrate = one gram of sample. Add hydrochloric acid to slight acid reaction, as shown by the disappearance of the rose color, and evaporate on a water-bath with platinic chloride. Wash the precipitate with alcohol, sp. gr. 0.848 (= eighty per cent. by weight), dry at 100° C., and weigh. For potash salts, the ignition with sulphuric acid is omitted.

Remarks: 1. The sulphuric acid must be added cautiously as fertilizers containing chlorides and nitrates react somewhat violently, endangering loss of the assay. 2. It is important that the ignited mass be very finely pulverized, otherwise the calcium sulphate, most of which remains insoluble, will mechanically enclose the potassium sulphate and prevent its complete

solution. 3. An excess of sodium carbonate is not permissible as double decomposition with the precipitated barium sulphate may take place, leaving sodium sulphate in solution and rendering erroneously high results. 4. It is recommended to turn the flame under the bath below boiling temperature when the solution has evaporated to small bulk. In case it then goes to hard dryness, no harm is done, while, if the bath be boiling, it is necessary to keep a close watch lest this occur. 5. For the filtration and weighing, a Gooch crucible, fitted with a single disk of filter paper, leaves nothing to be desired.

This method was first adopted as a safe one, on its favorable showing when checked against the Lindo-Gladding, and has since proven in the writer's hands very much more concordant than the latter. Since the publication of Mr. Norman Robinson's criticism of several well-known methods of potash determination (This JOURNAL, 16, 364), the writer has made a more careful investigation of the value of this process, comparing it with two others and incidentally confirming some of Mr. Robinson's work.

It was thought most satisfactory to operate on samples of known composition, and with this end in view several, representing the usual variety met with in commerce, were prepared. In each case the potash "occluded" by the various precipitates was determined after washing until no reaction with silver nitrate was visible. To facilitate comparison all the figures are given in per cent. potassium oxide.

Nature of Sample.	Calculated content potassium oxide.	Found by Lindo- Gladding.	Recovered; from precipitates.	Found by Stassfurt.	Recovered from precipitates.	Found by Garrigues.	Recovered from precipitates.
Complete Fertilizer; containing $K_2SO_4$ .	5.40	5.16	0.20			5.17	0.09
		5.28	0.11			5.19	0.12
						5.25	0.09
						5.28	0.17
Complete Fertilizer containing KCl.	6.31	6.12	0.15			6.22	0.08
		6.09	0.14			6.14	0.12
Mixed salts KCl+CaCl <sub>2</sub> + MgSO <sub>4</sub> .	63.17	63.19	0.12	62.85	0.19	62.75	0.18
		62.74	0.15	62.80	0.17	62.95	0.15

The figures under the headings of the three methods do not include the per cent. recovered from precipitates. In the Stassfurt method the quantity of barium chloride necessary was calculated and exactly added, so that no doubt need exist as to the potassium platinochloride obtained having been contaminated with sulphates on an excess of barium chloride. In one case the total return by the Lindo-Gladding method was apparently more than was present, due no doubt to a slight contamination with calcium sulphate. It should be remarked that no corrections were made for the volume occupied by the precipitates in the flasks. The factor used in calculating the double chloride to potassium oxide was 0.193.

The writer is frank to acknowledge that frequently the Lindo-Gladding method has given him very discordant results. This has been especially noticeable in fertilizers containing liberal amounts of potash. An aggravated case of the kind was a return in triplicate of 10.16-11.37-12.75. The writer's method gave 12.73-12.76 and an experiment station working on the same sample found 13.10. Two other instances of disagreeing duplicates by the Lindo-Gladding process are 4.76-5.07, and 6.10-6.54.

It is difficult to give any satisfactory reason for these discrepancies, as they are probably due to a multiplicity of causes. The writer has always felt the re-solution of the ignited potassium sulphate in water to be an unsatisfactory step and this alone sufficed to make the adoption of a new method desirable to him, the official alternate method being too tedious for ordinary use.

It is suggested that the material differences among chemists working by the Lindo-Gladding method, may be, in part, due to the varying strength of the alcohol-wash. The official directions, though they mention eighty per cent., do not lay sufficient stress on this point. If ninety, or even eighty-seven, be used in the second washing, ammonium chloride is precipitated with consequently higher returns.

In conclusion, while it is plain the method here proposed does not, in common with those now in use, return quite all the potash, it is seemingly less accurate than none and certainly less discordant than the Lindo-Gladding, besides being more satis-

factory to work, and quicker. It obviates the no small difficulty of precipitating all the sulphuric acid without adding an excess of barium chloride in the Stassfurt, and avoids the tedious evaporations and filtrations entailed by the alternate. Against all these advantages there has appeared so far only one disadvantage: the necessity of using a greater quantity of platinic chloride.

### THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK

BY W. D. HORNE, PH.D.

SEVERAL years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity.

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to three per cent.

In char, in constant use in sugar refineries, the moisture in the revived sample is of no importance under usual conditions.

The moisture is determined by heating two grams of the unground char for two hours in a hot air-bath at  $140^{\circ}\text{C}$ . It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grams of the finely pulverized sample are introduced into a two-ounce Erlenmeyer flask and moistened with three cc. of a saturated solution of mercuric chloride, the tube of ten cc. of hydrochloric acid (sp. gr. = 1.12) introduced and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample

<sup>1</sup> Read before the New York Section, November 9, 1894.

for analysis the iron particles must first be removed by a magnet and the char then ground to an almost impalpable powder.

Two grams of this are moistened with water and treated in a four-ounce covered beaker, with twenty cc. hydrochloric acid, and boiled gently until solution is complete, which is within thirty minutes. The beaker is filled up with boiling water and after settling, which takes place almost immediately, decanted upon a weighed platinum Gooch crucible with asbestos plug. The carbon is washed by decantation in this way five or six times, until the filtrate is free from chlorine. The original filtrate and first decanted washing contain practically all of the iron and calcium sulphate. The following wash-waters can usually be rejected. The carbon is washed out of the beaker into the Gooch, and is then washed with eighty per cent. alcohol, ninety-five per cent. alcohol and ether, each two or three times, set in a water-jacketed air-bath, and heated at  $100^{\circ}$  C. to a constant weight, which will take about three hours. The increased weight is due to carbon and ash. The carbon is burned off over the blast. The loss of weight is then carbon, and the difference is ash.

To the acid solution containing iron and calcium sulphate a drop of methyl orange solution is added and ammonia to nearly neutral reaction. Ammonium acetate is added until the solution turns yellow and then a few drops in excess. The solution is now heated below  $70^{\circ}$  C. until complete precipitation of iron and aluminum phosphate takes place, which is usually in about twenty minutes. The precipitate, after being washed free from chlorides, is dissolved by dilute sulphuric acid into a six-ounce Erlenmeyer flask, ten cc. of a ten per cent. solution of sodium sulphite added, and boiled to reduce the iron and to expel the sulphur dioxide. To ascertain when this gas ceases to come over, the vapor is led from the flask through a glass tube fitting through the rubber stopper and inclining vertically downward at its outer end. Under this is held a test-tube of dilute potassium permanganate acidified with sulphuric acid. So long as sulphur dioxide, issues it will decolorize the permanganate solution in the tube when the gas is caused to bubble up through the upper half inch of the solution. When the sulphur dioxide



is all out a drop of the solution from the flask is tested with potassium sulphocyanide for ferric iron. When the reduction is complete the solution is cooled and titrated with permanganate. If alumina is to be determined the above-mentioned precipitate of the iron and aluminum phosphates can be treated with 150 cc. of ammonium molybdate solution, to precipitate the phosphoric acid, and filtered. In the filtrate iron and alumina are precipitated as hydroxides by ammonia, filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, collected, ignited, and weighed. The two may then be separated by any of the well-known methods.

The filtrate from the iron and alumina precipitation contains the calcium sulphate. This solution is acidified with hydrochloric acid, and barium chloride added to precipitate the sulphuric acid. The barium sulphate is treated in the usual way and calculated to calcium sulphate.

Calcium sulphide may be determined by treating five grams of char with twenty cc. of nitric acid and evaporating nearly dry, adding twenty cc. of hydrochloric acid, and evaporating again very low to expel nitric acid, taking up in hydrochloric acid, and in an aliquot portion of the filtered solution precipitating the sulphuric acid in the usual way with barium chloride. From the weight of barium sulphate found, is deducted that found as above, due to calcium sulphate. The remainder is that due to calcium sulphide.

The physical condition of the char is of great importance and should be thoroughly examined into. The grist is estimated by throwing 100 grams upon a sieve of known mesh, shaking gently, and weighing what passes through. This portion may, in turn, be passed through successively finer sieves, and weighed after each. In shaking, the sieve should be tapped only very gently—otherwise particles of char will be forced through which, correctly, belong above.

To determine the density of the char it should be carefully filled into a weighed flask of 50 or 100 cc. capacity, and of very gently sloping sides. Admitted into such a flask through a funnel the char fills it completely without leaving vacant recesses at the shoulders. This is weighed, from which is cal-

culated the specific gravity of the char when loose and the pounds per cubic foot. Now the flask is tapped lightly on the table and as the char settles down more is added until no further settling takes place, and the flask is filled to the mark. This gives the weight of char when packed, from which may be calculated, as before, the specific gravity and weight per cubic foot.

As char grows old in use its porosity decreases and its specific gravity increases. It is sometimes desirable to know its porosity. To do this the weighed flask is filled with distilled water, the char introduced, little by little, displacing part of the water from the flask. At the same time the water remaining displaces from the char its contained air, which rises in minute bubbles. The flask is tapped to pack the char, and, when filled to the mark, is heated on the water-bath to expel all air. After cooling, the supernatant water is removed and the flask and contents weighed. The increased weight over that of the flask packed with char is that of the contained water, from which can be calculated the capacity of the char for any liquid of known specific gravity.

The repeated handling which bone-black receives in continued use in sugar refineries, etc., tells on it very seriously, as the friction of the grains against each other and the machinery wears it into dust. This change is slow, but in the long run is very costly, as the fine dust has to be discarded and replaced by new char.

Any method, therefore, which would enable one to judge of the relative durability of samples of char under this continued friction should be worthy of consideration. I have attempted to contrive such a test, and after a good many experiments have found one which promises well. Twenty-five grams of the char to be tested, between sixteen and twenty-four grist, approximately, are thrown on a sieve with circular holes, one-fiftieth of an inch in diameter, the sieve shaken back and forth ten times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron, four inches in diameter, and two inches deep; then six glazed porcelain marbles five-sixths of an inch in diameter and weighing together 74.66 grams are added. Now the can is shaken back and forth

with slightly rotary motion 200 times, the marbles removed, and the char sifted as before. The increased weight of dust is calculated to per cent. of the char used. These tests are pretty constant for different portions of the same sample of char.

The dust formed thus from a good new char was in three cases 1.72 per cent., 1.46 per cent., and 1.76 per cent. From another new char 2.68 per cent. and 2.44 per cent. Two grades made by one firm gave 2.16 per cent. and 2.16 per cent. in one case, and 2.86 per cent. and 2.87 per cent. in the other. Char which had been in use ten months and whose softer parts had already been separated by use gave 0.92 per cent. and 0.94 per cent., showing that it was then in a better wearing condition than when it first entered into use.

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### THE ASPHALT QUESTION.

By S. F. PECKHAM.

THERE has lately been published some very interesting reading concerning this question. To go back a few months, in October, 1892, Consul Pierce made a report that seemed to leave very little to be said in reference to Trinidad asphaltum from any standpoint. A few months later, Mr. Clifford Richardson published in the *Journal of Analytical and Applied Chemistry*, for Dec. 1892, and Jan. 1893, a paper in which he embodied the results of a most elaborate series of technical analyses of Trinidad asphalts. Within the last twelve months there has been published a voluminous report on Trinidad asphalt by Mr. Richardson, in the "Mineral Resources of the United States." In several late numbers of *Paving*, Mr. D. Torrey has shown that a method of analysis of asphalts may be based on successive solutions in alcohol; and he has also discussed in a very suggestive and intelligent manner, the general subject. In the July number of *Paving*, Messrs. Richardson and Bowen pay their respects to the report of Messrs. Leffman and Sadtler, made to the Citizens' Municipal Association and Trades League, of Philadelphia. In the August number of the same journal Messrs. Leffman and Sadtler reply to their critics. In the December number of this JOURNAL Miss Laura Linton publishes a paper, in which she gives the result of a very careful

research upon the methods heretofore employed in the technical analysis of asphalts. I am also just in receipt of a report upon "The Gas and Petroleum Yielding Formations of the Central Valley of California," by W. L. Watts, of the State Mining Bureau.

I propose, by a general review of these papers, to ascertain where a chemist, who is occasionally consulted in reference to asphalt, might reasonably take his stand.

It is now about fifty years since I first noticed, in a number of the *Penny Magazine*, an illustrated article on the "Pitch Lake of Trinidad." My interest in this wonderful phenomenon has never abated. Somewhere late in the fifties, when the Downer Kerosene Oil Co., was ransacking everywhere, but in Pennsylvania, for crude material for illuminating oil that was cheaper than Boghead Mineral, or Albertite, the late William Attwood was sent to Trinidad, where he remained two or three years. Several years after his return it was my good fortune to meet him, and I listened with eager interest to his description of the so-called lake, which he represented as a mass of asphaltum of unknown depth, floating upon a veritable lake of water. His experiments in the line of preparing illuminating oil from the asphalt were so far from a success that the late Samuel Downer once facetiously remarked, that the Trinidad pitch was, without doubt, derived from right-whales, black-fish, etc., while Pennsylvania petroleum was certainly nearly pure sperm oil. Later investigations have shown that both Mr. Attwood and Mr. Downer were considerably mistaken in their conclusions.

The report of Consul Pierce shows that the so-called pitch lake has no definite boundaries, but overflows towards the sea, over the rim of its irregularly circular basin, on one side. His report also shows that the sources from which the bitumen rises to the surface, are not confined to the strata beneath the so-called pitch lake, but are also found in the strata that underlie that portion of the island of Trinidad adjacent to the lake, to such an extent that unknown areas are covered with masses of asphalt, of unknown thickness. This asphalt, from both inside and outside the lake, was mined and sold, but that from outside the lake was finally distinguished as "land asphalt" by those who chose to

do so. Consul Pierce shows conclusively that the same cosmical forces that bring asphaltum to the surface in large quantity at the lake, bring it to the surface at many other points upon the island in smaller quantity, and, that other things being equal, the asphaltum is the same thing in both instances.

In Mr. Richardson's elaborate paper above referred to,<sup>1</sup> he gives results of analyses of a number of specimens that were taken from the lake, and compares them with corresponding results of analyses of a number of specimens taken from the land. He admits that no practical difference can be shown to exist between good commercial samples from either source; but he insists on introducing analyses of lake asphalt that are too soft for commercial purposes, and also of a lot of land specimens that, so far as serving any useful purposes are concerned, are neither more nor less than rubbish. No one familiar with deposits of surface asphalt in Southern California, would visit an asphalt bed and dignify the refuse from the numerous fires that, from immemorial periods, have swept over its surface, with the names of "iron-pitch," etc., and think an argument necessary to prove that the ashes, cinders, coke, and half-burned asphaltum, are unfit for street pavement. I have seen masses of coke, from fifteen to eighteen inches thick, taken from burnt asphalt beds, and thousands of tons of melted and half-burned asphaltum, in streams miles in length, the analysis of which would afford most convincing proof that they were unsuitable for street pavement. Setting aside the soft pitch on the one hand, and the rubbish on the other, it appears to me, that any unprejudiced person must admit, that Mr. Richardson's paper proves either too little or too much; either that the methods and material he used proves nothing, as is really the case, or that the results he has obtained prove the practical identity of "lake" and "land" asphalt of good commercial quality.

In the report by Mr. Richardson in "Mineral Resources of the United States for 1893," he goes into the history of the paving industry, and gives some very interesting details, both political and commercial, the argument of which appears to be that while there are other asphalt paving materials to be had in the

<sup>1</sup> *J. Anal. Appl. Chem.*, Dec. 1892, and Jan. 1893.

world, the only material worth considering is that laid by the Barber Asphalt Paving Co., that use and practically own the "lake" deposit, which, after all, is not a lake at all, but fills "the crater of an old mud volcano." He says, "in times past it appears that the continued welling up of pitch at the center of the lake filled the crater and caused it to overflow towards the sea." Here again, he either proves that the whole of the pitch is worthless, or that the whole deposit outside and inside the crater is practically one and the same thing.

He starts into the discussion of the Technology of Trinidad asphalt pavements, with the important information that "The crude pitch is shipped from La Brea in Trinidad in both sailing vessels and steamers." Farther on, he shows by a sort of historical résumé, that a little more care has lately been taken in refining the pitch than formerly, by which the damage resulting from prolonged overheating is avoided to some extent. He then grapples with the cement problem. He says of the fluxing oil, "it should not contain large amounts of hard paraffins, for in this case, while it may be of suitable nature for making cement at ordinary temperatures, it is susceptible to changes and makes the resulting cement too brittle at low temperature and too soft in heat of hot summer sun. The more the oil is of a vaseline nature the better it is. While the oil now in use is a great advance over that of some years ago, there still seems to be room for improvement. "The character of an oil may be learned by determining—

1. Specific gravity.
2. Flash-point.
3. Percentage volatile in seven hours at 400° F.
4. Susceptibility to changes in temperature as revealed in changes in viscosity.
5. Presence of crystals of paraffin scale.

Before mixing, the asphalt is raised to a temperature of 300° F., or thereabout, and to produce rapidly a smooth mixture, the oil should be heated as hot as is convenient. The oil is then pumped or in other ways added to the still, and the mixture agitated for several hours with a current of air until it is quite homogeneous. This agitation must be done with great thor-

oughness to insure a uniform cement, and must be continued whenever the material is in a melted condition, as a certain amount of separation takes place when the melted cement stands at rest. It is, therefore, customary to agitate it constantly with an air-blast when in use as well as in its preparation."<sup>1</sup>

Then he goes on to describe the ingenious toy with which Prof. Bowen, of Columbia College, amuses himself. This instrument is so delicate that, "as the needle (a cambric needle) is not at a normal temperature an allowance must be made." Comment is unnecessary.

In a paper that I read at the Congress of Chemists,<sup>2</sup> held at the Columbian Exposition, I took the position that the residuum in use for softening asphalt that is made from petroleums consisting of paraffins, and that consequently contains paraffins, is not a solvent for asphaltum, and therefore is not a suitable material for an asphaltic flux; as when an attempt is made to incorporate the two materials, the result is a mechanical mixture and not a chemical union as it should be. I based my argument on the results of laboratory experiments, and I now gladly welcome Mr. Richardson to my side, as his very emphatic statements are based upon the much stronger proof of practical experience. In the paper above referred to I further maintained that the custom of "blowing" asphalt, or mixing it by the use of a current of air injected into the molten mass while heated to a high temperature, is all wrong.

Mr. Richardson writes well, and he uses the word "scientific" in a way that sounds well; but I hazard the opinion, that if he read more and wrote less, his opinions would have more weight. The first "scientific" paper in which the effect of the prolonged heating of bitumens was discussed, was published by Boussingault in 1837. He says,<sup>3</sup> "after different experiments, the means that I have finally employed in order to free the bitumen of its volatile principles, consists in exposing it at a temperature of about 250° (C. = 480° F.?) in a Gay-Lussac oil-bath until it no longer loses weight. This method is prolonged, as it is necessary to heat during forty-five to fifty hours, even when operating

<sup>1</sup> *Mineral Resources of the United States*, 1893, 651.

<sup>2</sup> *Am. J. Sci.*, Jan., 1894; *Paving and Municipal Engineering*, Aug., 1894.

<sup>3</sup> *Ann. chim. phys.*, 64, 141.

on only two grams of material." In a note he adds, "By this method it is impossible to determine the two principles of the bitumen, as at that temperature a part of the petrolene is oxidized and passes to the solid state or asphaltene." Technologists in petroleum have known for years that prolonged heating will convert paraffin petroleums into a solid residuum. It has also been known for years that California petroleums can be so manipulated by heat as to convert a large percentage of them into an asphaltic residuum, that will contain varying proportions of material soluble in petroleum ether, carbon disulphide, and chloroform, leaving a residue of coke, according to the temperature to which it has been heated. The percentage of material soluble only in chloroform increases also in proportion to the time during which it has been heated. A patent has lately been issued from the U. S. Patent Office for a method or process for preparing these residues.

It seems incredible, that the scientific adviser of a great corporation, that has the reputation of seeking to control the asphalt paving business of the United States, should be ignorant of these facts. Why then this space occupied in the Mineral Resources of the United States, with descriptions of technological processes, that all of the knowledge possessed by the scientific world for the last sixty years, condemns as unscientific?

Mr. Richardson has taken great pains to show that he found a good quality of "land asphalt," that contained, if I remember his figures, two per cent. less of matter soluble in petroleum ether than a fair quality of "lake asphalt." This difference he regards as absolutely exclusive of "land asphalt" for paving purposes. He then describes how this "lake asphalt" is refined. He does not say whether refined lake and land asphalt differ by two per cent. of matter soluble in petroleum ether or not. He then shows how the refined lake asphalt is softened with a material that, according to his own showing, will not form even a mechanical mixture with the melted asphalt except by constant agitation with a current of air, and that, up to the point when the so-called cement is put into its final resting place upon the street. It is a fair question, whether lake asphalt after this wholly unscientific treatment does not contain a larger percentage of matter insoluble



ble in petroleum ether than would land asphalt, when properly manipulated.

Mr. Richardson says, " Washington has had more experience with sheet asphalt pavements and more time and attention have been devoted to both the scientific and practical sides of the industry there than in any other city in the country." If Mr. Richardson has faithfully represented the state of the art in this highly favored city, in what condition must the rest of the country be found where scientific principles have not been introduced into the industry?

Mr. Richardson has been giving his attention to the scientific principles underlying this industry for a number of years. I think it may be safely said that he has had a better opportunity to become an acknowledged scientific authority upon this subject than any chemist living. After what manner has he used this opportunity? He has published a large number of so-called analyses of asphaltum. When making these analyses he either found a method already in use, which his experience proved to be satisfactory, or he invented a better one. In either case, by long continued use, he made the method his own. I am not aware that he has anywhere described his method of analysis, but the terms in which he has stated the results of his analyses, indicate his method with sufficient clearness. He states the amount of water, the percentage soluble in petroleum ether, the percentage soluble in carbon disulphide, the percentage of organic matter not bitumen, and the percentage of inorganic or mineral matter. It is a fair assumption that with Mr. Richardson's opportunities, he thoroughly investigated every step in this process of analysis, and is prepared to show that water, and not volatile oils or gases, are determined as water; that either petroleum ether of any sp. gr., *e. g.*, any light distillate of petroleum can be used in place of any other, with the same results, or that a distillate of a particular sp. gr., obtained from a particular petroleum should be used. It is further to be presumed, that he is able to show that petroleum ether is the best liquid that can be used for this purpose, and that the separation made by its use is sharp and clearly defined. It is further to be

<sup>1</sup> Mineral Resources of the United States, 1897, 653.

presumed, that when this residue from which petroleum ether has made a complete solution, is subjected to the action of carbon disulphide, that setting aside the difficulty of obtaining the reagent pure, its action is attended with no serious objections and is complete; that is, it dissolves every trace of bitumen remaining in the residue. All of this should have been proved beyond question years ago. But Mr. Richardson has apparently allowed that two per cent. of difference between lake and land asphalt to so obscure his mental vision that he has left it to the careful and painstaking accuracy of Miss Linton to show that carbon disulphide will not dissolve completely the bitumen from asphaltum, and that boiling spirits of turpentine is an equivalent for carbon disulphide, and is a much more convenient and satisfactory reagent to use.<sup>1</sup>

There are mistakes to which every one is liable and that are properly to be excused; there are others that are absolutely without excuse. I confess, that to my mind, there is no excuse for a man, who, occupying the position or responsibility that Mr. Richardson has occupied, publishes the results of analyses year after year, upon which, as a basis, it has been sought to influence the expenditure of millions of public money, when, in reality, he has made no proper investigation of his processes, and knows nothing respecting the accuracy or proper significance of his results. Mr. Richardson has no right to complain if his constituency hereafter repudiate all of the dicta that he has with, I had almost said, unpardonable arrogance thrust upon the public, in reference to the "Asphalt Question."

I have read the articles of Mr. Torrey with a great deal of interest.<sup>2</sup> They are suggestive. I have not found, by experience, that his method of analysis by solution in alcohol, promises any superiority over that proposed by Miss Linton. The test of a method of analysis is, other things being equal, the parallelism shown in the results when duplicate analyses are made, side by side. In one instance, with her process, I have obtained results parallel to the third place of decimals. Such close correspondence in work of this kind is not generally to be expected;

<sup>1</sup>This JOURNAL, 16, 809.

<sup>2</sup>*Paving and Municipal Engineering*, Nov., 1893; April, May, and September, 1894.

but the process, on the whole, has given me very satisfactory results, and the possibility of rejecting altogether the use of carbon disulphide is a great gain.

Messrs. Sadtler and Whitfield, remark in their article in *Paving*, "While some of the European asphaltic limestones are capable of being used for paving without addition of fluxing material, they have not been found to make as satisfactory pavement as those containing a siliceous base."<sup>1</sup> Why should they? Is not any form of calcium carbonate easily dissolved by rain-water or decomposed by weak acids, such as abound in the street gutters? Will Mr. Richardson please explain why pulverized limestone is required as an ingredient of the asphalt surface used in Washington? Why is it any better than the same amount of fine quartz sand? The reasons given above are sufficient reasons why it is not as good. In California, infusorial earth occurs in many localities in close proximity to deposits of asphalt. It is found to be a very superior material with which to temper asphalt.

On page 52 of the Report of the California State Mining Bureau, above referred to, an extract appears from the Records of the Standard Asphalt Co. There an attempt is made to compare some of Mr. Richardson's analyses of Trinidad asphalt, made with petroleum ether, with other analyses made by G. Q. Simmons, who analyzed California asphalt by using common ether. Other tests are given, made by H. Stillman, who used presumably petroleum ether from California petroleum. Miss Linton has shown that the solvent powers of these three reagents, when applied to the same asphaltum, vary widely; hence they can not be used interchangeably, and results based upon their use can not be compared. The material used should be petroleum ether of sp. gr. 700 equal to 70° B., obtained from petroleum consisting of hydrocarbons of the marsh-gas series—in other words "paraffins."

These criticisms have not been made at the suggestion of, or in the interest of any party to the asphalt question.

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.,  
October 30, 1894.

<sup>1</sup> Ibid, September, 1894, 120.

## QUICK ESTIMATION OF STARCH.

BY P. L. HIBBARD.

Received November 3, 1894.

THE accurate estimation of starch in presence of crude cellulose or similar substances containing other carbohydrates soluble in hot water or boiling dilute acids, has not yet been accomplished. Lintner's process of heating in closed vessels under high pressure, with water or a weak acid, like tartaric, *e. g.*, is good when soluble convertible carbohydrates other than starch are absent. Märcker's process of dissolving the starch out of the fiber by means of diastase is also fairly satisfactory. But both methods will bring into solution more or less of the various gums, etc., which are nearly always present in starch-bearing material. Entirely to avoid solution of these bodies is, so far, impossible; but it is certain that the less the material is heated with water, or especially with acid, the less will they be dissolved. Perhaps the best method published is Märcker's. The substance is boiled with water a few minutes to gelatinize starch, then cooled to 60° C., some diastase added, and the whole heated on the water-bath at 65° C. for one hour, to hydrolyze the starch. The solution is then filtered from the insoluble residue and converted by hydrochloric acid to dextrose, which is then determined by Fehling's solution. All the directions that I have seen, say the mixture must be heated with diastase for one hour, and then it must be heated two or three hours on a water-bath, with a reflux condenser. A modification of this method consists in heating the substance under pressure of three atmospheres, with lactic or tartaric acid, after the first treatment with diastase. The acid is then neutralized and the whole again warmed with diastase. The conversion to dextrose is as before stated. These methods are somewhat long and tedious, besides being liable to bring into solution other bodies than starch, which, by the subsequent process, will reduce Fehling solution.

Whole corn, soaked a few minutes, was stripped of its hulls. These hulls were carefully examined to see that they were free from starch and were not colored by solution of iodine. After

boiling them a few minutes with water, the solution was filtered off and heated with acid a short time. It then reduced Fehling solution somewhat. This experiment shows that mere boiling with water brought into solution some body, which was converted by acid into a reducing sugar.

Having occasion to estimate starch in residues containing much of other soluble carbohydrates, I have modified the method using diastase, so that it is much shorter and easier, as well as fairly accurate. The method is satisfactory for factory work, where great accuracy is not so necessary as speed; and slightly modified is the most accurate method known.

Instead of taking trouble to prepare diastase by precipitating and washing with alcohol, I make a water extract of malt, which answers well. The coarsely pulverized dry malt is covered with water containing fifteen to twenty per cent. of alcohol. After a few hours the infusion is filtered off and is ready for use. The sugar in this must be determined by treating with acid as described below, in order to make the correction due to it when used to dissolve starch. The alcohol to some extent prevents action of the diastase on the starch of the malt, but is chiefly useful to preserve the malt extract, which would ferment very soon if some antiseptic were not present. Twenty per cent. of alcohol will preserve it for two weeks, even in very warm weather. I have found no effective preservative, except alcohol, that does not destroy the diastatic power of the malt extract.

The substance in which starch is to be determined should be finely pulverized, in order that the starch may be easily extracted without long boiling. Enough of the material to contain at least half a gram of starch is placed in a flask with about fifty cc. of water and one or two cc. of malt extract added. The mixture is at once heated to boiling, with frequent shaking to prevent formation of clots of starch. The addition of diastase before gelatinizing the starch, helps to prevent formation of insoluble clots, as it acts above the temperature at which starch becomes pasty. But if the material contains little starch in presence of much fibrous material, there is no particular gain in adding malt before heating to boiling, as

most of the diastase is destroyed by the high temperature, before it has time to act on the starch. After boiling a minute the mixture is cooled to  $50^{\circ}$ – $60^{\circ}$  C., and two to three cc. malt extract added. Then it is heated slowly from ten to fifteen minutes till boiling, again partially cooled, and tested with iodine solution. If there is blue, the treatment with malt must be repeated. When all the starch is changed, the mixture is cooled, made up to definite volume, and filtered. I have found fine muslin or linen a very satisfactory filter for this purpose. Though it does not at first filter quite so clear as paper, it is more rapid, not being so easily clogged when the substance is albuminous. The cloth retains all the fibrous material, which might give rise to sugar in the subsequent treatment with acid. An aliquot part of the filtrate, sufficient to contain two or three-tenths of a gram of starch, is placed in a 100 cc. flask with five cc. HCl containing thirty per cent. of acid gas, and water to make about sixty cc. total. This is boiled moderately thirty minutes actual boiling, on a sand-bath. This gives complete conversion. I use a sand-bath and no condenser, as the amount evaporated from a narrow-necked flask in this time is not enough to make much difference. If a water-bath is used longer time is required. The solution is now cooled, nearly neutralized with sodium hydroxide, and the dextrose determined by Fehling solution. With pure starch the solutions obtained are almost colorless, but if the substance contains much albuminoid matter, which will be destroyed by the acid, the solution will be brownish. There is no apparent destruction of sugar in this length of time.

The action of various acids on starch has been investigated by F. Salomon, (*J. prakt. Chem.*, **28**, 82,) and it is concluded that hydrochloric is the best acid to use in the hydrolysis of starch. Less than an hour of moderate boiling with the strength of acid above given is sufficient to convert starch directly without previous solution with diastase. Much longer heating destroys sugar and the solution becomes brown.

The residue left after treatment of a good quality of starch by this method is little, but some of it is soluble in dilute acid, so that direct conversion with acid gives a little higher figures, but

it seems probable that this is largely due to other bodies than starch. I have made many experiments to determine the proper time and best strength of solutions, and find the above given most satisfactory.

This method is simple, rapid, and fairly accurate. A determination of starch may be easily finished in less than two hours. Particular points are: prevention of insoluble clots by addition of malt before heating; the rapid heating prevents any lactic fermentation which may occur in the use of the older published methods; and the little boiling occasions a minimum solution of bodies other than starch, which could form reducing sugars. With nearly pure starch there is no occasion for use of this method. The process is valuable chiefly for estimating starch in presence of much other material which may give rise to reducing sugars by the action of acid, *e. g.*, fodders, cattle foods, and residues from starch manufacture. A sample of corn hulls, free from starch, gave only a trace of sugar by this method, but direct conversion with acid showed forty per cent. of reducing sugar.

The appended figures show the errors due to the acid method, and afford a comparison of the two:

Material.	Moisture in sample.	PER CENT. STARCH.	
		Malt method.	Acid direct.
Starch factory feed.....	10.0	10.0	40.9
Impure moist starch.....	12.0	81.3	82.3
Impure moist starch.....	...	79.5	80.9
Good starch.....	12.8	84.3	84.6
Purified dried starch.....	...	95.1	96.5
Corn, large white kernels.....	11.0	63.5	68.2
Wheat, hard red variety.....	10.0	60.5	65.0
Bran from same wheat.....	11.3	28.4	44.4
Middlings from same wheat.....	10.1	53.8	60.0
Low flour from same wheat.....	10.2	66.0	67.7
Good flour from same wheat.....	11.0	67.9	69.0
Wheat flour.....	10.0	70.7	73.6
Wheat bran.....	10.1	29.3	46.5

The method may be further improved and each chemist's needs will indicate to him useful modifications. Others may make it more perfect, and to them I commend it as the most promising method for determination of starch.

Most of the careful analytical work in the investigation of the method was done in the laboratory of the University of Nebraska, for the use of which I am indebted to the kindness of Professor H. H. Nicholson.

LABORATORY OF THE ARGO MANUFACTURING COMPANY,  
NEBRASKA CITY, NEB., November 1, 1894.

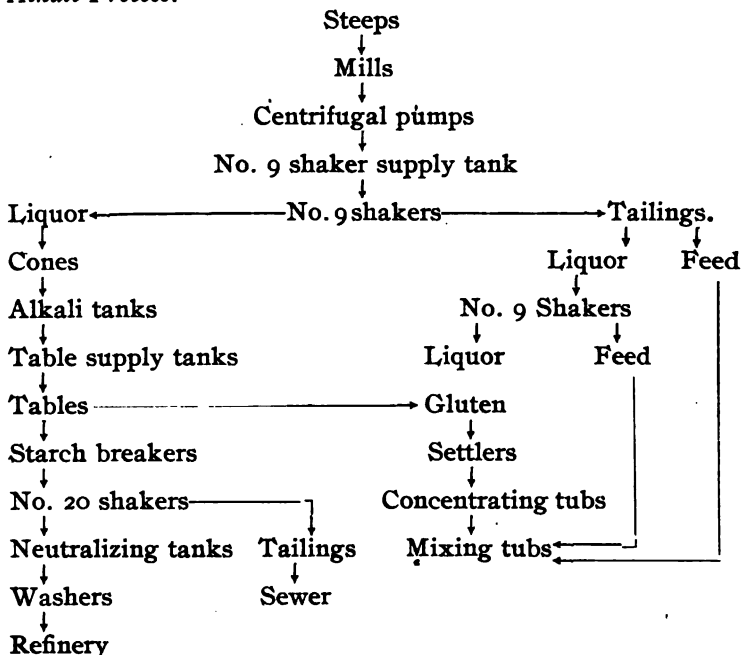
## ALKALI AND SULPHUROUS ACID PROCESSES USED IN THE MANUFACTURE OF STARCH FROM CORN.

BY HORACE E. HORTON.

Received September 19, 1894.

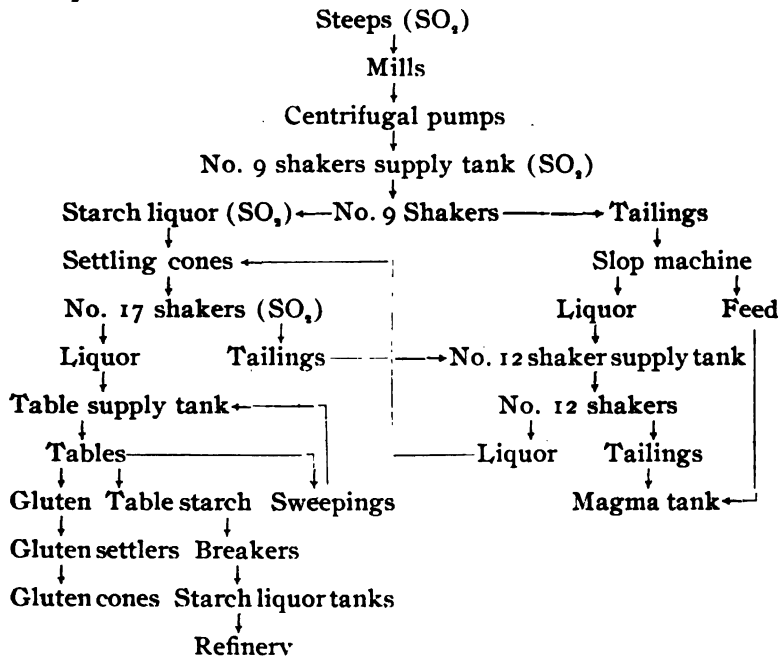
**S**TARCH is produced from corn at the present time by two processes, known as the alkali and sulphurous acid. I am not aware, at this moment, of the existence of any published article showing the working of these processes, and I take pleasure in presenting two outlines, showing clearly, and at a glance, their essential points.

### *Alkali Process.—*





*Sulphurous Acid Process.*—



classified together systematically, which is by no means an easy task. This has been accomplished by arranging them in the first part of the book, under the following heads: Analysis by Neutralization, Precipitation, Oxidation, Indirect Oxidation (Iodometry), and Analysis of Easily Reducible Substances.

Following a general introduction, accompanied by complete directions for using apparatus, each class is introduced by a clear exposition of its principles, and in addition each assay is treated in a uniformly explicit manner. In some instances other methods are added to those official, as for example, Stolba's method to determine phosphoric acid, Personne's method for valuing potassium iodide, or Kingzett's method to determine the available oxygen in hydrogen dioxide. An excellent feature is, that with each reaction the equation and molecular weights involved are also given, the equivalent weights entering into the percentage calculation being deduced therefrom and stated.

Thus in each assay the operator finds the work a complete guide, nothing being left to conjecture or research, each subject being complete in itself, and hence Part 1st of the book becomes a systematic commentary on the assay methods of the U. S. P.

Part 2nd embraces manipulations of a more elaborate nature, such as the Assay of Opium, Cinchona, Ipecac, The Valuation of Pepsin and of the Resinous Bodies in Jalap and Scammony. These are of great value to pharmacists, and it is to be regretted that in this direction Prof. Schimpf did not enlarge upon the U. S. P. It is needless to state that in such cases gravimetric methods are employed. Attention may be called to the introduction of the methods of Benedict and Sigmundy for estimating glycerol, and of Loewenthal for tannin in barks, these being omitted in the U. S. P., and also to directions for the Volumetric Analysis of Sugar, Urine, Starch in Cereals, Alcohol, Milk, Butter, Fats in Ointments, and numerous others not mentioned in the U. S. P.

Part 3rd is devoted to Gasometric Analysis, and the estimation of Spirit of Nitrous Ether, Hydrogen Dioxide, etc., by the Nitrometer. The Appendix considers Indicators, Reagents, and Test Solutions.

This book is well illustrated and invaluable both to pharma-

cists and to chemists interested in assaying. It is an outgrowth of the Pharmacopeia and the reviewer regrets that space does not permit him to dwell at greater length on its excellent features. Every volumetric method of the Pharmacopeia is recorded explicitly with the one exception for oleic acid in which the process of Muter's Chemistry is substituted, being an improvement, however, in that the assay introduced determines oleic acid in the presence of stearic and palmitic acids which the method of the U. S. P. does not accomplish.

Notwithstanding that such a variety of subjects are embraced and condensed in a comparatively small volume, superficiality can not be charged against it. The book enables the reader, even though he has but a limited training in chemistry, to comprehend and at once carry out each assay described. It should be in the hands of every pharmacist.

J. U. LLOYD.

A TEXT-BOOK OF INORGANIC CHEMISTRY. BY G. S. NEWTH, F.I.C., F.C.S. pp. xiii; 667. 146 Illustrations. London and New York: Longman's, Green & Co. 1894. Price, \$1.75.

To those who have learned to appreciate the value of Newth's "Chemical Lecture Experiments," the announcement of a complete text-book by the same author, will certainly be a matter of interest. Lecturers on experimental chemistry have found the "Experiments" a most helpful guide, replete with clever, ingenious, practical devices for the lecture table, placing at the instructor's service all the latest mechanical and electrical adjuncts, and substituting for many of the antiquated illustrative features, modern striking forms of experimentation.

The same characteristics are to be encountered in the new work, freshness in material and treatment, numerous illustrations, novel and suggestive, replacing many of the time-honored wood-cuts of the standard text-book.

The author's arrangement of matter is a deviation from all the customary methods. He divides his work into three quite distinct parts. Part I—"Introductory Outlines." 150 pages are devoted to theory and chemical physics, notation, nomenclature, atomic weights, valence, heat, pressure, electrolysis, solutions, thermo-chemistry, periodicity, etc. This whole section is

marked by great clearness of presentation and accuracy of statement.

Part II. "The Study of Four Typical Elements." 150 pages are devoted to quite an exhaustive treatment of hydrogen, oxygen, nitrogen, and carbon, with their more important compounds. This section unfrequently recalls Hofmann's famous "Einleitung" where likewise a few elements are utilized to bring out the main essentials of chemical fact and theory. Especially noteworthy in this part is the admirable treatment of *flame* and *combustion* thoroughly up to the times, and far in advance of any existing text-book treatment of these important topics.

Part III. 350 pages are devoted to the remainder of the elements, following closely the periodic classification. The space given each element is necessarily somewhat limited, sodium, for example, receiving but twelve pages, magnesium, four pages, etc. Here we notice, however, as a rule, that the work is well up to the times, notably in technical manufacturing processes. Geographical reference is almost entirely omitted, with some rare exceptions, as in the case of mercury.

Just what is the most advantageous arrangement of the matter in a text-book of this size, is a moot question. Among recent works we find on the one hand Mixer's, adhering rigidly to the periodic classification, and on the other hand Freer's, following the same classification after a study of oxygen, Remsen's doing likewise after a study of oxygen, hydrogen, and chlorine, while, as we have seen, Newth prefaces the same classification with a study of four elements, and prefaces the latter also with an extended section on theoretical and physical chemistry. From my own experience and observation I am inclined to the opinion that the brighter, more persevering students in a college class make satisfactory progress with any of these types, while, on the contrary, a considerable number can profitably take up such a text-book as Newth's only after preliminary drill in some one of the excellent elementary works introducing theoretical concepts gradually, with the acquisition of the necessary experimental facts.

While recognizing fully the many excellent qualities in Dr. Newth's work, attention should be called to several of those

deficiencies which are almost inevitable in an author's first edition. Thus while there is an excellent chapter on thermochemistry in the introduction the subject is almost entirely ignored in the treatment of individual elements and compounds, although in so many cases (as in that of the allotropic forms of phosphorus) it serves admirably to explain important facts.

Uniformity and simplicity in nomenclature are frequently neglected. Note, for example, the following two headings of sections within a few pages of each other: (1) *Arsenuretted Hydrogen* (*Arsenic Trihydride*, *Arsine*), and (2) *Antimony Hydride* (*Antimoniuretted Hydrogen*).

The space assigned individual metals seems frequently too brief; and despite the author's excuse in the preface, I can not approve of the very step-motherly treatment in a book of nearly 700 pages, of the so-called rare metals. Titanium, which is so important to the metallurgist and which forms a larger percentage of our planet than does carbon, receives four lines. Zirconium, cerium, and thorium are passed by with the same meager mention, although their oxides are now in every-day use in our homes for illuminating purposes. This latter fact is omitted entirely, while mention is made of the now much less extended employment of lime for similar purposes. Tungsten, molybdenum, and uranium receive together but one page.

While, as already stated, the work in most instances is quite up to the times—for example, in the account of the lately discovered new element in the atmosphere—still in certain cases there is an inexcusable lack of recognition of recent fact and method.

Thus, under aluminum, we find but a single method of preparing the metal. The historically interesting process of St. Clair Deville receives over a page of description. But not a gram of aluminum is made to-day by that method. That more and more valuable servant of the modern chemist, electrolysis, is granted in fact but scant attention. While a brief allusion to the action of the current on sodium chloride is found in the preface, no mention is made of the important reaction in connection with either chlorine or with sodium compounds. Similarly, while fourteen different methods for preparing oxygen are described in detail, not a word is given to the simplest and most

elegant of all, the reaction between water and sodium peroxide, now employed in every laboratory and lecture-room. No mention is to be found of red fuming nitric acid.

The date of 1876 for Moissan's discovery of free fluorine is probably a typographical error.

T. H. NORTON.

DIE MASCHINELLEN HILFSMITTEL DER CHEMISCHEN TECHNIK. von Alwin Parnicke. pp. 320. 327 Illustrations. H. Bechhold, Frankfurt, A. M. 1894.

The lack of a good manual on the methods used for the mechanical preparation of substances used in the chemical industries to which Mr. Pemberton has already called attention in these columns, (see this JOURNAL, 1893, p. 634) is supplied in the excellent digest of the subject contained in this book. The sections into which the book is divided may be translated as follows: 1. Sources of Power. 2. Transmission of Power. 3. Methods of Transportation. 4. Grinding. 5. Mixing. 6. Melting, Dissolving, and Extraction. 7. Concentration. 8. Mechanical Separation. 9. Drying. 10. Weighing, Determination of Temperature, Pressure, and Draught. 11. Laws Relating to the Subject.

The book is well printed and the illustrations are excellent, an important matter in such a book. It is to be hoped the book may find a translator who will condense it sufficiently for class use.

E. H.

THE ELEMENTARY NATURE OF CHLORINE. BY HUMPHRY DAVY, SEC. R. S., 1809-1818. PAPERS PUBLISHED IN THE PHILOSOPHICAL TRANSACTIONS. ALEMIC CLUB REPRINTS, No. 9. 80 pp. Edinburgh: William F. Clay. 1894.

This reprint is no less interesting than its predecessors. The first three papers give the results of experiments made to determine the properties and composition of "muriatic acid." In the remaining six papers Davy describes a few experiments by other chemists and many of his own upon "oxymuriatic acid," discusses them and, without asserting that this gas is an element, suggests that it be called chlorine, on account of its color and because it "is not known to contain oxygen and can not contain muriatic acid." A short account of the discovery and properties of "Euchlorine" is found in one of the papers.

L. B. HALL.

# THE JOURNAL

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### A MODIFIED ARRANGEMENT OF THE ELEMENTS UNDER THE NATURAL LAW.

BY F. P. VENABLE.

Received December 22, 1894.

A quarter of a century has passed since the first announcement of the Natural Law and the publication of Mendelejeff's table. The truth of the law, in a general way, seemed to be accepted very readily by chemists. It was incorporated in text-books and there explained, but comparatively little use has been made of it in teaching the science. Even Mendelejeff himself, in his *Principles of Chemistry*, has not made the fullest use of it. Victor Meyer, in his lecture before the German Chemical Society more than a year ago, showed how it might be used, and how he used it himself, and, probably, this will do much towards popularizing its use.

There must be some reason why so great a help to scientific study, is not made more use of. Does it lie in a lingering distrust of the law itself or failure to accept it, or is it because of the imperfections in the arrangements of the elements offered by Mendelejeff and others? It is most probably due to the latter, and this paper is presented with the hope of clearing up some of these difficulties.

The modern chemical world has recognized in the discovery of Mendelejeff, the greatest step forward since the announcement of the Atomic Theory. It is too much to expect that so great a discovery should spring full-panoplied from the head of its author.

Doubtless many have observed the imperfections of the law's original form, or rather the table as first given out. Probably some have ventured to comment upon it. Such criticisms have, however, escaped me with one or two exceptions. It is with much hesitation, that I venture to point out what seem to me imperfections and blemishes, in so great a work. Few may agree with me in calling them imperfections. I do not purpose to detract one particle from the greatness and importance of the essential truths contained in this discovery. Mendelejeff's table, as we have it at present, is a great advance upon the first one published by him in 1869, which must be pronounced tentative only, and decidedly unsatisfactory. The table of Victor Meyer is far behind it in presenting the facts of the periodic law. There have been many attempts at devising a graphic representation of this law. I know of none which can be called a real aid to the student, or which do not introduce new ideas which, to say the least, have no basis in the facts as known to us at present. None of them can be regarded as a safe substitute for the simple table of Mendelejeff.

Taking this table I would venture to point out some obstacles to its full acceptance. These have been in part revealed to me by the effort at a presentation of these truths of nature to honest-minded, clear-sighted young men.

Before mentioning the difficulties which lie here in the path of a teacher, I must say, by way of preface, that my criticisms, are aimed at what I may be allowed to call the unessentials of the law. Mendelejeff's great feat was in seeing clearly, and announcing intelligently, that the properties of the elements are dependent upon and determined by the atomic weights. This is the essential of the Natural Law and is in accord with our fullest knowledge. The second part of the law, as usually stated, that these properties are periodic functions, attempts, in a measure, to define the dependence. It may also be true, but it is not fully proved and it is open to objections. It seems to me that this hypothetical portion could well be left in abeyance until fuller knowledge gave it a stronger footing, meanwhile substituting something less open to criticism, and which can not weaken the central truth.



TABLE I.

Group.	I	II	III	IV	V	VI	VII	VIII
Series I	H	—	—	RH, RH,	RH, RH,	RH, RH,	RH	{Hydrogen compounds.
" 2	Li .	Be .	B .	C .	N .	O .	F .	Fe. Co. Ni. Cu
" 3	. Na .	. Mg .	. Al .	. Si .	. P .	. S .	. Cl .	
" 4	K .	. Ca .	. Sc .	. Ti .	. V .	. Cr .	. Mn .	
" 5	. (Cu) .	. Zn .	. Ga .	. Ge .	. As .	. Se .	. Br .	
" 6	Rb .	. Sr .	. Y .	. Zr .	. Nb .	. Mo .	—	Ru. Rh. Pd. Ag
" 7	. (Ag) .	. Cd .	. In .	. Sn .	. Sb .	. Te .	. I .	
" 8	Cs .	. Ba .	. La .	. Ce .	. Di? .	—	—	—
" 9	. —	. —	. —	. —	. —	. —	. —	Os. Ir. Pt. Au
" 10	—	. —	. Yb .	. —	. Ta .	. W .	. —	
" 11	. (Au) .	. Hg .	. Te .	. Pb .	. Bi .	. —	. —	
" 12	—	. —	. —	. Th .	. —	. U .	. —	
	R <sub>2</sub> O —	R <sub>2</sub> O, RO	R <sub>2</sub> O, —	R <sub>2</sub> O, RO,	R <sub>2</sub> O, —	R <sub>2</sub> O, RO,	R <sub>2</sub> O, —	Higher Oxides. RO,

TABLE II.

Groups.	Higher salt-forming oxides.	Typical, or first small period.	Large periods.				
			1st.	2nd.	3rd.	4th.	5th.
I .....	R <sub>2</sub> O	Li 7	K 39	Rb 85	Cs 133	—	—
II .....	RO	Be 9	Ca 40	Sr 87	Ba 137	—	—
III .....	R <sub>2</sub> O <sub>3</sub>	B 11	Sc 44	Y 89	La 138	Yb 173	—
IV .....	RO <sub>2</sub>	C 12	Ti 48	Zr 90	Ce 140	—	Th 232
V .....	R <sub>2</sub> O <sub>5</sub>	N 14	V 51	Nb 94	—	Ta 182	—
VI .....	RO <sub>3</sub>	O 16	Cr 52	Mo 96	—	W 184	U 240
VII .....	R <sub>2</sub> O <sub>7</sub>	F 19	Mn 55	—	—	—	—
VIII .....	{		Fe 56	Ru 103	—	Os 191	—
			Co 58.5	Rh 104	—	Ir 193	—
I .....	R <sub>2</sub> O	H = 1	Ni 59	Pd 106	—	Pt 196	—
II .....	RO	Na 23	Cu 63	Ag 108	—	Au 198	—
III .....	R <sub>2</sub> O <sub>3</sub>	Mg 24	Zn 65	Cd 112	—	Hg 200	—
IV .....	RO <sub>2</sub>	Al 27	Ga 70	In 113	—	Te 204	—
V .....	RO <sub>3</sub>	Si 28	Ge 72	Sn 118	—	Pb 206	—
VI .....	R <sub>2</sub> O <sub>5</sub>	P 31	As 75	Sb 120	—	Bi 208	—
VII .....	RO <sub>3</sub>	S 32	Se 79	Te 125	—	—	—
	R <sub>2</sub> O <sub>7</sub>	Cl 35.5	Br 80	I 127	—	—	—
		2nd small period.	1st.	2nd.	3rd.	4th.	5th.

Take the tables from the first volume of Mendelejeff's Principles of Chemistry and examine them. First, we find two kinds of periods made use of—periods containing seven elements, and those containing seventeen. These latter are divided into sevens and threes. If it had only been possible to arrange all of the elements in sevens, as Newlands attempted to do, the periodic idea would have been most convincing, and the Law of Octaves, running through nature, would have seemed most wonderful. But these elements do not admit of being arranged in this way, and the use of periods of different lengths, is to a fresh young mind, unacquainted with mathematical expedients, somewhat forced.

Secondly, there is a very anomalous position assigned to the triads, or as sometimes written, the tetrads, Fe, Co, Ni, Cu, etc. They have been set off to themselves, clearly so as to make the other elements fall, even approximately, into their places, and into the proper sevens. I say approximately, for the student soon sees that although there is a similarity, there is also a wide difference between the elements of the first seven and the last in any period of seventeen.

Thirdly, in the lower periods, in order to get elements to fall into their places, a great many unknown elements have to be interpolated. Thus between cerium and ytterbium, the next element in the list, there are blank places for sixteen elements. The third large period of seventeen has only four known elements in it, and the fifth has only two. That means that here we have a period actually constructed out of fifteen unknown elements and two known ones. This exceeds some of the triumphs of geology in the construction of skeletons of extinct animals. Of the five periods, only one is completely filled out. To say the least, this shows a very imperfect knowledge of the elements, or a great deal of guess work. In the table there are sixty-four known elements and thirty-five blanks for elements yet to be discovered. I hardly think it possible that the majority of chemists, believe that, after all of the diligent search for the past century, less than two-thirds of the elements have been discovered. Where are the others in hiding? Will they be discovered by the spectroscope among the rare earths? There is certainly hope of finding some of them there, but the number which this

statement of the law would require us to find, is simply appalling. The average student thinks, in all honesty, that the coincidences of the first part of the table, will scarcely justify such forcing and wholesale interpolation. If our knowledge of the elements be so imperfect as that, we have no right to force them into periods, in fact, any law based upon their atomic weights would be of the most tentative character, and likely at any time to be overthrown by the discovery of the lost or unknown ones. How do we know that the big one-third, now unknown, may not upset all calculations, when found? Such a law ought rather to be called a working hypothesis. We are venturing a great deal upon a very imperfect knowledge of the ones we have in hand. For if one reckons up the number of elements, for which we have satisfactory determinations of the atomic weights, he will find that they are less than forty. The periodic idea may be true, but we do not know enough about these elements yet, to be able to give this idea a very prominent place in the Natural Law, and we ought to avoid the assumption of so many unknown elements unless it is absolutely necessary.

As I do not intend to tear down without some effort at rebuilding, I would, with much real diffidence, for I realize that I may be looked upon as one who would rush in where only the great masters of the science can safely tread, offer the following suggestions.

The first suggestion is that the wording of the Natural Law be so changed as to read: "The properties of the elements are dependent upon and determined by the atomic weights." The somewhat difficult idea of functions is simplified and periodicity is subordinated. Then the following table might be substituted for the one ordinarily given.

It is not greatly changed and not much originality is claimed for it, but, however slight the changes, I would insist upon their value, because they do away with the dependence upon periods and they certainly make the table easier, more intelligible, and more useful to the student. No very doubtful element is included in it. There is room for additional elements as discovered, but the table is not dependent upon them. Lastly the inter-relation is more clearly brought out.

TABLE III.

			RH,	RH,	RH,	RH		
			RO,	RO,	RO,	RO,		
			R <sub>2</sub> O,	R <sub>2</sub> O,	R <sub>2</sub> O,	R <sub>2</sub> O,		
Li	Be	B	C	N	O	F		
Na	Mg	Al	Si	P	S	Cl		
K	Cu	Zn	Ga	As	Se	Br	Fe	Co
Rb	Ag	Cd	In	Sb	Te	I	Ru	Rh
Cs	Au	Hg	Tl	Pb	Bi	U	Os	Ir
	Ba	La	Ce	Ta	W			Pt
			Th					

I do not maintain that this table could ever have been discovered without the idea of periods, though I can see no reason why it might not. The periods still underlie it, but they are out of sight for the present, and are not necessary. The table is not dependent upon them.

The table is constructed as follows. There are seven group elements, having a mean increment of two in their atomic weights. It is by no means essential that there should be just seven of these. At present we do not know more, but I think there is possibly a place for one more, having the atomic weight twenty-one and differing widely from the others as it occupies a singular position.

These group elements are also to be called bridge elements, as they show marked gradation of properties from one to another and serve to bridge over the groups and connect one with the other. Linked to them by an increment of sixteen, are seven typical elements. These show the distinctive properties of the groups to which they belong and a wider divergence from the next group to them. From them can be deduced the properties of the remaining elements of the group. Thus, in group I, Li is the bridge or group element, and Na the type. From this type two lines of elements diverge, averaging three to the line. These triads would, of course, be changed into tetrads or pentads by the discovery of more elements. No importance can be attached to the fact that at present they are triads. There is a distinct increment for each line of elements. These can be averaged thus:

Fig. 1.

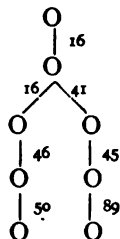


Fig. 2.

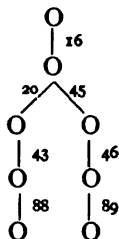


Figure 1 represents the arrangements and increments for the first three groups, and figure 2, that in the last four groups,

the increments showing a variation. These increments could be averaged in all except one case, and the agreements with known atomic weights would be close enough to admit of the easy arrangement of the elements in the prescribed order. Naming the triads right triad and left triad, respectively, we find that these averaged increments would be as follows: The increment from group to type element is sixteen; from type to first element in left triad is eighteen; to second element in left triad is sixty-three; to third element in left triad is 112. On the other side to first element in right triad is forty-four; to second element in right triad is eighty-nine; to third element in right triad is 177.

The one exception mentioned is in the increment from type to third element in right triad, in groups IV to VII. Instead of being 112, the increment here is 141.

To the right of group VII we have three triads which have the regular increments belonging to the left triads, namely, forty-seven and eighty-eight. They are without any type element. It seems most likely that they belong to one group. The group element would have an atomic weight of twenty-one, and the type one of thirty-seven.

The arrangement in the table then, is partly one based upon regular increments in the atomic weights, and, since these weights are but poorly known, partly upon our knowledge of the properties of the elements. When it is recalled that about one-half of the atomic weights are imperfectly known, it will be evident that these averaged increments are approximations only. It is impossible to bring out such perfect symmetry as is obtained in the homologous series in organic chemistry. And yet these groups should be something of the same kind. Following the analogy to the organic hydrocarbons a little further, may not the existence of an element in two different conditions as to valence, etc., as, for instance, copper, or mercury, or iron, be looked upon as a species of isomerism? Such speculations are of little use, however, and quite apart from our present purpose. I have found this table very useful in teaching elementary chemistry, and it can most profitably be made the basis of the entire course. Thus, in the first four groups, the left triads contain

the elements most closely resembling the types. In the last three they are to be found in the right triads. As to natural occurrence of the elements, in the first four groups those in the left triads occur in the same compounds, and generally in connection with the type; those in the right triads occur as the type, or as sulphides, or free. In the last three groups this is reversed. The right triad elements occur as the types, and the left triad elements as the type or as oxides. So, too, the properties of the elements show this relation to the types. Take as an example the specific gravities in group II.

Be = 2.1	
Mg = 1.75	
/ \	
Ca = 1.5	Zn 6.9
Sr = 2.5	Cd 8.6
Ba = 3.6	Hg 13.6

It is not necessary to pursue this part of the matter at greater length. The careful teacher will easily work out all of these comparisons for himself, and will find that chemistry taught by the table is shorter (so much repetition being saved) and is easier for the pupil, and its symmetry and beauty are much more easily brought out. There is no special claim for originality made here. The germs of such a table, or arrangement, can be found in several text-books, but I do not know of any in which the idea is fully developed, or such a table as this is given.<sup>1</sup> I offer the whole as a suggestion. Perhaps some may find it useful who have met the same difficulties which I have encountered. Others may have overcome these difficulties in a still better way than this. I think, at least, all will agree that there are difficulties, and very serious ones, in the use of Mendelejeff's table, or that of Victor Meyer, as given by their respective authors.

<sup>1</sup> The arrangements of Bayley, Hinrichs, and Wendt are somewhat similar, but the ideas which I would make prominent, are obscured by other considerations and speculations.



## THE DETERMINATION OF POTASH IN KAINITE.

BY RUDOLF DE ROODE.

Received December 12, 1894.

**A**N aqueous solution of kainite contains nothing except potash which, upon evaporation with platinum chloride, forms a compound which is insoluble in alcohol and the ammonium chloride wash ordinarily used in potash determinations. It is, therefore, quite superfluous to precipitate out anything from such a solution by such reagents as barium chloride, ammonium oxalate or carbonate, etc., and to evaporate and ignite the residue obtained. A most accurate result is obtained by evaporating an aliquot portion of a filtered aqueous solution of kainite directly with platinum chloride. Upon the addition of alcohol to the residue obtained by evaporation, nearly to dryness, with platinum chloride, the sodium sulphate present renders the potassium platinochloride sticky and difficult to wash, just as in the Lindo-Gladding method. The sodium sulphate is readily washed out with the ammonium chloride wash, however, leaving a pure potash double salt. The method of direct evaporation of a solution of kainite with platinum chloride has the advantage that there is no loss from occlusion or retaining of potash by precipitates, since no precipitants, such as barium chloride, ammonium oxalate, etc., are used. There can also be no loss from spattering, volatilization, etc., upon ignition, since no ignition is used. Using the same aqueous solution of a sample of kainite, and making determinations by the Lindo-Gladding, the Alternate, and the Stassfurt methods, and also by direct evaporation with platinum chloride, I obtained the following results:

Lindo-Gladding .....	12.36	per cent.	potassium oxide.
Alternate.....	12.42	" "	" "
Stassfurt .....	12.40	" "	" "
Direct evaporation with platinum chloride .....	12.54	" "	" "

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
December 10, 1894.

**THE OXIDATION OF ORGANIC MATTER AND THE DECOMPOSITION OF AMMONIUM SALTS BY AQUA REGIA, IN LIEU OF IGNITION, IN THE DETERMINATION OF POTASH IN FERTILIZERS.**

BY RUDOLF DE ROODE.

Received December 12, 1894.

IN the determination of potash in fertilizers errors may arise, by reason of a loss of potash, when the residue obtained upon evaporation is ignited to destroy organic matter and to drive off salts of ammonium. Such loss may easily occur, either by spattering or a mechanical carrying off of potassium sulphate by the voluminous fumes of sulphuric acid used in the Lindo-Gladding method. In the alternate method, a loss of potash may occur by reason of direct volatilization. Extreme care must be exercised in the ignition, both in the Lindo-Gladding, and in the alternate method, in order to obtain accurate results.

In order to avoid the errors which might arise from such ignition, and, in fact, to do away with the necessity for any ignition whatever, I tried the action of aqua regia. J. Lawrence Smith has shown that salts of ammonium are readily destroyed by aqua regia, and it is well known that organic matter is oxidized thereby. I found, upon evaporating a solution of a mixed fertilizer, prepared as in the Lindo-Gladding method, with nitric and hydrochloric acids, that the salts of ammonium were completely destroyed, and that the organic matter was either entirely destroyed, or else so highly oxidized that it no longer exercised a reducing action upon platinum chloride.

By preparing a suitable solution of a fertilizer and evaporating an aliquot portion of this solution with aqua regia, we ought, therefore, to obtain a residue quite as well adapted to the determination of potash by platinum chloride as a residue obtained by evaporation and ignition.

The *details* of a method for the determination of potash in fertilizers, based upon this principle, have not yet been thoroughly worked out. Some excellent results have been obtained and

some results which were not so good, but, on the whole, the method is quite promising and will be the subject of further study by me, which I trust may result in a somewhat more accurate and more convenient method than those now in general use.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
December 10, 1894.

### ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.

BY J. H. LONG.

Received December 19, 1894.

I HAVE elsewhere called attention to the behavior of solutions of tartar emetic when treated with solutions of other salts, (see *Am. Jour. Sci. and Arts*, October, 1889 and October, 1890) and with Mr. H. E. Sauer have determined the conditions of precipitation by carbonates, acetates, and phosphates. (*J. Anal. Appl. Chem.*, March, 1891.)

When to solutions of the antimony salt sulphates, chlorides, nitrates, and oxalates of the alkali metals are added no precipitation occurs, even with elevation of temperature. With carbonates, acetates, phosphates, borates, thiosulphates, sulphites, tungstates, and some other compounds, clear solutions can be made at a low temperature, but precipitation follows at a higher point. The precipitate, in nearly all cases, consists of hydrated antimony oxide, and its amount is a function of time, temperature, and amount of added salt.

With mixtures of the tartrate and sodium carbonate, for instance, it was found that in the cold, at the end of twenty-four hours, amounts were precipitated as shown in the following table. In each test five grams of the tartrate were dissolved in sixty cc. of warm water and cooled to 20°. Then different weights of pure sodium carbonate were dissolved in thirty-five cc. of water; these solutions were added to the others and the mixtures were brought up to 100 cc. They were allowed to stand until precipitation was complete, usually over night or longer. An aliquot part of the clear supernatant liquid was

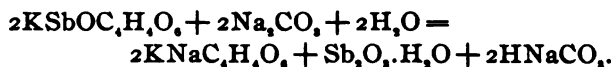
taken and the amount of antimony in solution determined. This was calculated to tartrate in the whole:

No. of experiment.	Na <sub>2</sub> CO <sub>3</sub> added.	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · $\frac{1}{2}$ H <sub>2</sub> O left in solution.
1.....	0.1 gram	99.93 per cent.
2.....	0.3 "	85.22 " "
3.....	0.5 "	70.36 " "
4.....	0.7 "	56.76 " "
5.....	0.9 "	40.87 " "
6.....	1.2 grams	29.17 " "
7.....	1.5 "	13.94 " "
8.....	2.0 "	3.88 " "

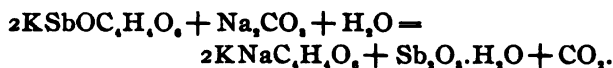
In another series of experiments the solutions of carbonate and tartrate were mixed as before at 20° and then brought to 100°, and maintained at this heat one hour. The precipitates formed immediately, and at the end of the hour were separated by filtration. The filtrates were tested for antimony remaining. The results are shown in the third column below.

No. of experiment.	Na <sub>2</sub> CO <sub>3</sub> added.	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · $\frac{1}{2}$ H <sub>2</sub> O left in solution.
9.....	0.2 gram	79.23 per cent.
10.....	0.5 "	46.70 " "
11.....	0.8 "	21.74 " "
12.....	1.1 grams	8.69 " "
13.....	1.5 "	6.33 " "
14.....	2.0 "	4.42 " "
15.....	3.5 "	4.66 " "
16.....	5.0 "	4.74 " "

On comparing the two tables, it will be seen that at first the precipitation is much more rapid in hot solution than in cold, but that finally, with excess of carbonate, a more complete decomposition of the tartrate is effected in the cold solution. Two equations can be given, according to which the reaction may take place. The first of these is:



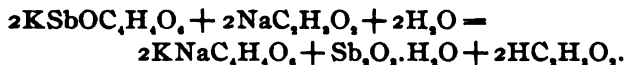
The second is:



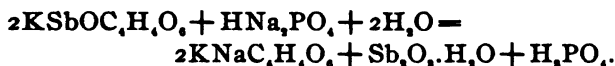
The first, probably, takes place in the cold solution as no carbon dioxide escapes. The loss of carbon dioxide from the hot

solution is less than called for by the equation because an excess of neutral carbonate is present and the solutions are not actually boiled. In any case the precipitation is incomplete, and by addition of increased amounts of sodium carbonate, a condition is reached in which a part of the oxide at first thrown down appears to go into solution again.

Precipitation with sodium acetate takes place imperfectly in the cold, but by heat a stronger reaction follows. In both cases it was found that the results may be expressed by the following equation :



With phosphates the experiments led to the conclusion that precipitation takes place in a manner represented by this equation :



With cold solutions precipitation is very slow, but by heat an amount of the antimony oxide corresponding to seventy-five per cent. of the tartrate originally in solution is obtained.

I have since investigated the behavior of several other salts as precipitants, with the results which follow.

#### REACTION WITH SODIUM BIBORATE.

A very sharp reaction takes place between solutions of borax and tartar emetic, which was studied in the following manner: In the first series of experiments, five grams of the tartrate were dissolved for each test in sixty cc. of water, the solutions being brought to 20°. To these were added definite weights of borax dissolved in thirty to thirty-five cc. of water at the same temperature. The mixtures were made up to 100 cc. exactly, and allowed to stand over night in a place with nearly constant temperature. In all cases a precipitate formed which was separated by filtration. The analysis of the precipitate showed it to have the same composition as that formed by the sodium carbonate; *viz.*,  $\text{Sb}_2\text{O}_3 \cdot \text{aq}$ . On drying at a high temperature most of the water is lost, leaving practically  $\text{Sb}_2\text{O}_3$ .

In each case the precipitate was separated by filtration, and

the filtrate made up to 250 cc. Twenty-five cc. of this was taken and precipitated by hydrogen sulphide, after addition of tartaric and hydrochloric acids in small amount. The precipitation was finished on a hot water-bath, and the precipitate collected on a Gooch filter, washed, dried at  $120^{\circ}$ , and weighed. The sulphide was calculated to tartrate on the supposition that all the antimony in solution was left in the original form ( $\text{Sb}=\text{120}$ ,  $\text{O}=\text{16}$ ). The results obtained are shown by these figures:

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
1.....	0.1 gram	98.81 per cent.
2.....	0.2 "	94.74 " "
3.....	0.4 "	87.78 " "
4.....	0.8 "	74.98 " "
5.....	1.6 grams	46.84 " "
6.....	3.2 "	3.31 " "

In another series of tests the solutions containing the borax and tartrate were made up to 250 cc. instead of to 100 cc. They were allowed to stand, filtered, and treated as before, giving these results:

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
7.....	0.1 gram	100.00 per cent.
8.....	0.2 "	97.15 " "
9.....	0.4 "	89.05 " "
10.....	0.8 "	75.29 " "
11.....	1.6 grams	49.09 " "
12.....	3.2 "	6.01 " "
13.....	6.4 "	2.03 " "
14.....	12.8 "	0.99 " "

In a third set of experiments the liquid containing the borax and tartrate was diluted to 100 cc. in a flask, as in the first set. The flask was closed with a perforated rubber stopper having a long glass tube attached, and then heated in boiling water one hour. The liquid was allowed to cool, was filtered, and the filtrate made up to 250 cc. An aliquot part, on analysis, gave results which are shown below.

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
15.....	0.1 gram	99.88 per cent.
16.....	0.2 "	95.37 " "
17.....	0.4 "	88.81 " "
18.....	0.8 "	74.78 " "
19.....	1.6 grams	47.03 " "
20.....	3.2 "	3.96 " "
21.....	6.4 "	1.76 " "

In these tables several things are immediately apparent. It appears that the precipitation is less perfect in hot solution than in cold, although for equal weights of borax the differences are not great. It is seen also that the amounts precipitated are greater in the strongest solutions. These effects of temperature and concentration are far less marked, however, with borax precipitation than with that by the sodium carbonate.

With borax we have, in each case, a very regular rate of precipitation. By plating the weights of borax in the above table as abscissas, and the amounts of tartrate left as ordinates, we obtain a curve which is almost a straight line.

It seems practically impossible to precipitate all the antimony by excess of borax, although the amount left in solution is much less than when sodium carbonate was used as the precipitant. Direct trials showed that the solubility of the antimonous oxide in excess of borax solution is very slight, but is a trifle greater in the excess of sodium carbonate. The solubility in the Rochelle salt solution formed in the latter case will not account for this difference as will appear below.

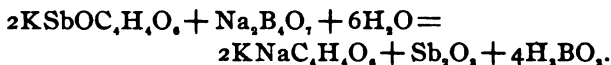
In order to gain further insight into the reaction I measured the amount of rotation of polarized light in a number of solutions before and after the separation of the precipitate of antimonous oxide. Some exceedingly interesting results were obtained, a few of which will be explained in detail. I dissolved five grams of the tartrate in fifty cc. of hot water and added three grams of borax in twenty-five cc. of water, made up to ninety cc., and heated one-half hour in the water-bath. The solution was allowed to cool to 20° and made up to 100.5 cc. (on account of volume of precipitate), and filtered through a dry filter. The filtrate was polarized in a 200 mm. tube, giving

$$\alpha_D = 3.596^\circ.$$

Seventy-five cc. of the filtrate, after the addition of a little hydrochloric and tartaric acids, was precipitated by hydrogen sulphide. The precipitate was collected, washed, and dried in the usual manner in the Gooch funnel. I found 0.119 gram of the sulphide, corresponding to 0.312 gram of  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , in the whole filtrate. 4.688 grams had, therefore, been precipitated. From the outset it would naturally occur to one that the

precipitation of antimonous oxide must be accompanied by the formation of sodium potassium tartrate, and that the polarization effect observed must, in part, be due to this, as well as to the potassium antimonyl tartrate left. I have elsewhere given the results of very accurate tests in which the rotation constants of these tartrates were determined by the use of the large Landolt-Lippich polarimeter with the 400 mm. tube (*Am. Jour. Sci. and Arts, loc. cit.*). From these it appears that the rotation of 0.312 gram of the  $\text{KSbOC}_2\text{H}_4\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and 3.982 grams of  $\text{KNaC}_2\text{H}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$  (this latter corresponding to the tartar emetic decomposed) in 100 cc. should not be over  $2.6^\circ$ . In the direct polarization of the filtrate I found, as given above,  $3.596^\circ$ . It is evident, therefore, that something else must be present to modify the result.

It is well known that the presence of boric acid increases the rotation of tartrates in a marked degree, and this can be readily accounted for here if we assume that the reaction takes place according to the following equation:



On applying tests for free boric acid its presence was readily shown. We have here apparently a reaction similar to those in which acetic and phosphoric acids are liberated from acetates and phosphates.

In the last experiment it was shown that antimony, corresponding to 0.312 gram of the potassium antimonyl tartrate was still in solution, or that 4.688 grams had been decomposed. To do this according to the above equation would require 2.697 grams of crystallized borax, and would leave in solution 3.982 grams of  $\text{KNaC}_2\text{H}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$  and 1.751 grams of  $\text{H}_3\text{BO}_3$ . An excess of 0.303 gram of borax would be left in solution. To test the correctness of this view I prepared a solution containing in 100 cc., at  $20^\circ$ :

0.312 gram of  $\text{KSbOC}_2\text{H}_4\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ .  
 3.982 grams of  $\text{KNaC}_2\text{H}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$ .  
 1.751 grams of  $\text{H}_3\text{BO}_3$ .  
 0.303 gram of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .



This solution was polarized in the 200 mm. tube and gave

$$\alpha_D = 3.590^\circ,$$

which agrees very well with the result of the first experiment. Another solution, containing in 100 cc., at  $20^\circ$ ,

0.150 gram of  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,

4.119 grams of  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ,

1.811 grams of  $\text{H}_3\text{BO}_3$ ,

gave  $\alpha_D = 3.661^\circ$ . While boric acid increases the rotation of tartrates and tartaric acid I have elsewhere shown that borax decreases the rotation of Rochelle salt slightly. The equation probably represents the facts properly.

In the above nothing has been said about certain peculiarities observed in the formation of the precipitates. When cold dilute solutions of borax and the tartrate are mixed no reaction takes place immediately, but with warm, strong solutions, a precipitate seems to form as soon as the two liquids are poured together. In a former paper (*J. Anal. Appl. Chem.*, *loc. cit.*) I pointed out the important and exceedingly curious fact that in the reaction between carbonates or acetates on the one hand, with the tartrate on the other, while no precipitate may appear immediately, perhaps not in hours, indicating a decomposition, the polarimeter shows that such has taken place. Here, also, we have evidence that a reaction has taken place even without precipitation, and this the polarimeter furnishes. The matter can be best explained by giving the details of several experiments.

I made five solutions by dissolving five grams of the tartrate as before in fifty-five to sixty cc. of warm water, cooled to  $20^\circ$ , and added certain weights of borax in small volumes of water, making the solutions finally to 100 cc. at  $20^\circ$ . These solutions were polarized immediately in the 200 mm. tube, with the following results:

No. of experiment.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ taken.	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ added.	$\alpha_D$
1.....	5 grams	0.5 gram	12.08°
2.....	5 "	1.0 "	9.40°
3.....	5 "	2.0 grams	5.53°
4.....	5 "	3.0 "	4.10°
5.....	5 "	4.0 "	3.75°

The normal rotation of the tartrate at  $20^{\circ}$  in the 200 mm. tube, with a concentration of five grams in 100 cc., I have shown to be

$$\alpha_D = 14.103^{\circ}.$$

The effect of the borax is therefore marked, but the extent of the decrease in rotation depends on the number of minutes intervening between the mixing of the solutions and the completion of the observation in the polarimeter. A gradual decrease in the readings was in all cases observed, until the solutions became finally too turbid for observation from the beginning precipitation. The first solution, for instance, in the above table was read as follows:

10 hours, 30 minutes,	$\alpha_D = 12.08^{\circ}$
10 " 45 " "	" = 11.87^{\circ}
10 " 55 " "	" = 11.80^{\circ}

After standing some hours, the solutions deposited a precipitate and cleared up. On again polarizing I found:

No.	$\alpha_D$
1.....	11.52^{\circ}
2.....	9.01^{\circ}
3.....	5.29^{\circ}
4.....	3.92^{\circ}
5.....	3.65^{\circ}

These observations were made in a 200 mm. tube, but similar solutions were polarized in a 400 mm. tube with perfect sharpness, the readings agreeing within  $0.02^{\circ}$ , as is possible with the large and excellent instrument used. I mention this to prove the perfect transparency of the liquids, and to show that the decreased rotations observed at the start were not due to any loss through precipitation, but were in consequence of changes preceding precipitation, these changes taking place very gradually.

We have here a phenomenon reminding one of the birotation of solutions of certain sugars, but depending on a different cause undoubtedly. In the reaction between the same tartrate and sodium carbonate the same change was observed, but through a longer period. A solution containing in 100 cc. one-tenth gram of the carbonate and five grams of the tartrate gave, at the end of five minutes in a 400 mm. tube, a rotation of  $25.582^{\circ}$ , after

thirty minutes,  $25.580^\circ$ , that is, practically the same, but after twelve hours,  $24.480^\circ$ . A perfectly clear mixture can be made containing five grams of the tartrate and nine-tenths gram of sodium carbonate in 100 cc. When polarized immediately, I found with this in the 400 mm. tube  $\alpha_D = 11.57^\circ$ , after ten minutes,  $11.50^\circ$ , after twenty-five minutes,  $11.132^\circ$ , and after sixty-five minutes,  $10.55^\circ$ .

In the normal reaction between carbonates or borates and the potassium antimonyl tartrate a precipitate should be formed, but we find that at a low temperature this is much delayed. If precipitation alone were taken as the indication of a reaction it would necessarily appear that at the outset no reaction takes place, but the behavior with polarized light shows the error in this view. It is evident that a reaction begins immediately and progresses far toward completion in some of the cases considered before even the first polarization can be made, that is within two or three minutes. This first part of the reaction is the beginning stage of precipitation and may consist in the formation of some intermediate product, which finally decomposes. I have elsewhere shown (*Am. Jour. Sci. and Arts, loc. cit.*) that the rotation of potassium sodium tartrate is decreased by the addition of sodium, thallium, and lithium salts, but is increased by the addition of potassium and ammonium salts and that this reaction is fully accounted for if we assume the formation of sodium tartrate, sodium thallium tartrate or sodium lithium tartrate in the one case or of potassium or potassium ammonium tartrate in the other. In the present instance we evidently must admit the formation of sodium potassium tartrate from the instant the solutions are mixed, but that the reaction is a progressive one. The potassium antimonyl compound with a high rotation gives place to the potassium sodium compound with a much lower rotation. There is nothing to show, however, in what form the antimony is held.

Possibly the reaction may be explained by assuming the formation of an intermediate product according to this equation :



If the last compound is broken it must break up in this manner :



leaving a hydrated oxide of antimony with more water than the final precipitate contains. By loss of water, possibly, this hydrated compound must, in time, settle out as a precipitate. It has been explained that by boiling, the precipitate forms and subsides soon. At  $20^{\circ}$ , even after what I have called the preliminary stage of precipitation, may have occupied hours, the actual formation of the precipitate may consume an equally long time. The precipitate is a growth through an invisible and a visible stage, and what is true here is true of the next case to be given.

#### REACTION WITH SODIUM TUNGSTATE.

Cold solutions of the tartrate give no immediate precipitate when mixed with cold solutions of ordinary sodium tungstate, but on standing the mixtures gradually become turbid and finally deposit a sediment. The composition of this depends largely on the temperature and concentration. The precipitate formed in the cold, collected and dried at  $105^{\circ}$ – $110^{\circ}$  C. consists, essentially of antimony oxide. A precipitate formed by mixing hot solutions has practically the same composition, but if obtained after long heating it contains a relatively larger amount of tungstic acid.

In a series of tests made by mixing hot solutions of the two salts, and allowing the mixtures to stand several hours to cool, the following results were obtained :

$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 100 cc.	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 50 cc.	Wt. of ppt.	$\text{Sb}_2\text{S}_3$ from same.	Per cent. of Sb. in ppt.
1 gram	2 grams	0.3087	0.3467	80.22
2 grams	2 "	0.6442	0.7291	80.84
4 "	2 "	0.5728	0.6486	80.88
5 "	2 "	0.7222	0.8170	80.79

The mixtures were made in platinum dishes holding about 200 cc., and as the precipitates formed as a coherent coating on the dishes they were easily washed, dried at  $110^{\circ}$ , and weighed. They were then dissolved in diluted hydrochloric acid, which left a small amount of tungstic acid in each case in flocculent form. The solutions were then filtered, and, after the addition of some tartaric acid, were precipitated by hydrogen sulphide in the usual manner. The sulphide precipitates were collected on a Gooch, dried at  $110^{\circ}$ , and weighed. It will be seen that the

results are a little low to correspond to pure antimony oxide as the composition of the white precipitate. This compound contains 83.3 per cent. of antimony. The compound  $\text{Sb}_2\text{O}_3 \cdot \text{H}_2\text{O}$  contains 78.4 per cent. The lower results are doubtless due to the small amounts of tungstic acid left in each case on treatment with hydrochloric acid, and referred to above.

In a second series of experiments constant amounts of the tartrate in hot solution were mixed with varying amounts of the tungstate likewise in hot solution. The white precipitates which formed were collected and weighed as before, with the following results, which show the effect of excess of tungstate on the amount of precipitate. In each case two grams of the tartrate was taken in 100 cc., and the tungstate in fifty cc.:

Tungstate taken.	Ppt. obtained.
0.5 gram	0.1070
1.0 "	0.4598
2.0 grams	0.5762
3.0 "	0.5861
4.0 "	0.6143
5.0 "	0.6185

From this, it is plain that the amount of precipitate is not much increased by great excess of the tungstate beyond a certain point. In the cold, precipitation is much less perfect, while, by boiling, fully three-fourths of the theoretical yield of oxide from the tartrate can be obtained.

By working with cold solutions a mixture may be made which remains clear long enough to permit polarimeter observations to be taken. I dissolved five grams of the tartrate in sixty cc. of water, cooled to  $20^\circ$ , and added five-tenths gram of the tungstate in twenty cc. of water. The mixture was made up quickly to 100 cc. at  $20^\circ$  and polarized in the 200 mm. tube immediately and after intervals of five minutes. I found without refilling the tube:

1st observation	$\alpha_D = 11.66^\circ$
2nd "	" = $12.03^\circ$
3rd "	" = $12.13^\circ$
4th "	" = $12.53^\circ$

The solution became now too turbid, from separation of a precipitate, for further tests. On standing some hours the remainder

of the solution in the flask cleared after subsidence of its precipitate. A portion of this examined gave

$$\alpha_D = 12.74^\circ.$$

Another portion of the same solution, heated and then cooled to  $20^\circ$ , gave the same. A new solution prepared in the same manner gave, after standing some time,

$$\alpha_D = 13.11^\circ.$$

I made next a solution containing in 100 cc. five grams of the tartrate and one gram of the tungstate. This examined, immediately, at  $20^\circ$ , gave

$$\alpha_D = 9.42^\circ,$$

but it soon became turbid and deposited a precipitate. After clearing, I found

$$\alpha_D = 11.48^\circ,$$

which increased to  $11.87^\circ$  by heating the liquid.

These reactions are especially interesting when compared with those between the tartrates and other salts. We have here, as before, a marked decrease in the specific rotation on mixing the solutions of the active and inactive substances. But in the case of the tungstate, on standing, there is an increase instead of a decrease in the rotation observed in the other cases. This behavior finds its explanation probably in the action of the liberated tungstic acid. The reaction between the two salts undoubtedly follows this equation :



The precipitation of the tungstic acid is very slow and incomplete. While in solution, it may combine with the soluble tartrate to form a body with increased rotation, the possibility of which is shown by the researches of Gernez and others. The delay in the appearance of the precipitate may be due to the formation and slow breaking up of intermediate products containing the antimony and tungstic oxides in temporarily soluble condition. With liberation of the tungstic acid we have a gradual increase in the already decreased rotation. This change in the rotation, before precipitation, is well shown in the following observations. I dissolved five grams of the tartrate and two and five-tenths grams of the tungstate, mixed at a low tempera-

ture and made up to 100 cc. as before, and at exactly 20° C. A reading with the 200 mm. tube was made as soon as possible and, without changing the solution, this was repeated at frequent intervals. The results were as follows :

3 hours, 28 min.  $\alpha_D = 5.66^\circ$

" =  $5.96^\circ$

" =  $6.45^\circ$

" =  $6.83^\circ$

" =  $7.15^\circ$

" =  $7.32^\circ$

3 hours, 44 min. " =  $7.43^\circ$

3 hours, 58 min. " =  $7.90^\circ$

At this point the liquid began to grow slightly turbid, so that the observations could not be continued. The remainder of the liquid was then heated in a closed flask to complete the precipitation, cooled to 20°, and tested. I found now

$$\alpha_D = 9.13^\circ.$$

The liquid still remaining was filtered, fifty cc. of the filtrate taken and precipitated with hydrogen sulphide, yielding finally 0.4045 gram of antimony sulphide. From this it appears that of the tartrate originally taken, 1.599 grams remained in solution in the 100 cc. (no allowance being made for the volume of the precipitate).

From this we have

$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$  decomposed = 3.401 grams.

" " remaining 1.599 "

$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$  formed 2.888 "

Now, the rotation corresponding to the tartar emetic remaining is  $4.50^\circ$  and that to the Rochelle salt formed is  $1.25^\circ$  from which we should expect a total rotation of  $5.75^\circ$ . This, in fact, corresponds very nearly to what was observed at the beginning of the test, and seems to bear out the suggestion made above: *viz.*, that the principal reaction here occurs before actual precipitation appears. A splitting of the tartar emetic is indicated by the immediate decrease in the rotation and then the complex effect of addition of the liberated tungstic acid to the alkali tartrate in solution appears from the gradually increased rotation

Precipitation finally follows as the end of the reaction; the separated part assumes the insoluble form.

It will be recognized that the phenomenon in this case is much more complex than in the other. There is nothing to show that while the rotation is being increased by the action of the tungstic acid there is not also a tendency toward decrease because of progressive decomposition of the potassium antimonyl tartrate. In all probability the observed rotation is a resultant effect.

#### REACTION WITH SODIUM THIOSULPHATE.

Cold dilute solutions of the thiosulphate and potassium antimonyl tartrate can be mixed without immediate precipitation. Application of heat, however, produces a light yellow precipitate which grows deeper and finally becomes bright red. This precipitate is the substance commonly known as antimony cinnabar, used as a pigment, and on the large scale is made by decomposing the thiosulphate by antimony chloride. In the reaction between the thiosulphate and tartar emetic the precipitate appears very heavy, but the decomposition is far from complete as shown by the figures given below.

There seems to be some doubt as to the composition of this precipitate. Roscoe and Schorlemmer (2, part 2, 324) give it as, probably,  $\text{Sb}_2\text{S}_3\text{O}$ , referring, however, to other formulas. Dammer's Handbuch gives  $\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{S}_3$  as the probable formula. Others are also given. Recently Baubigny (*Compt. rend.*, No. 17, 1894), has given reasons why the formula  $\text{Sb}_2\text{S}_3$  should be considered the correct one and the proof he presents appears to be satisfactory. There remains a possibility, however, that the composition may, under certain circumstances, vary with the method of preparation. In fact, some of my own results seem to show this and I am now engaged in studying the question further. But as made in the reaction in hand the composition seems to be  $2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$ . This was determined by the following considerations: The precipitate dissolves in hydrochloric acid without liberation of sulphur, yielding a perfectly clear solution. A solution made in this way was heated, mixed with a little tartaric acid solution, and precipitated by hydrogen sulphide in the usual manner. On filtering off the orange-yellow precipi-



tate so obtained in a Gooch crucible, drying at  $120^{\circ}$ , and weighing, the weight was always found less than that of the antimony cinnabar taken.

Sulphur determinations were made by dissolving a gram or less of the substance in strong S-free solution of potassium hydroxide and then oxidizing the sulpho-salt formed by washed chlorine gas, (method of Rivot). The results of these tests were as follows:

	Calculated for $2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$ .	Found.
Sb.....	69.56	69.80
S.....	27.83	27.72

No determination of the water was made, but its presence was shown in the substance dried at  $120^{\circ}$  by heating to a higher temperature in a narrow glass tube.

In a series of experiments on the precipitation a number of portions of the tartrate, of five grams each, were weighed out and dissolved in 150 cc. of water. Varying amounts of the thiosulphate in fifty cc. of water were added and then water enough to make exactly 250 cc. The flasks holding the mixtures were closed with perforated stoppers containing long glass tubes and then heated in the water-bath one hour. In this way evaporation was practically avoided. At the end of the hour the precipitates were collected on a Gooch funnel, dried at  $120^{\circ}$ , and weighed with the following results:

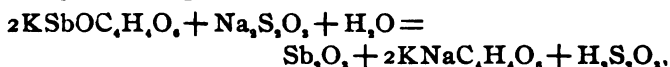
No. of experiment.	Weight of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ added.	Weight of precipitate.
1.....	0.1 gram.	0.0039 gram.
2.....	0.2 "	0.0068 "
3.....	0.4 "	0.0111 "
4.....	0.8 "	0.0178 "
5.....	1.6 grams.	0.0363 "
6.....	3.2 "	0.0803 "
7.....	6.4 "	0.2112 "
8.....	12.8 "	0.4809 "

In a second set of tests I dissolved, in each case, ten grams of the tartar emetic in 100 cc. of hot water and added the thiosulphate in fifty cc. of hot water. The mixtures were kept at  $100^{\circ}$  two hours and then filtered. Results as follows:

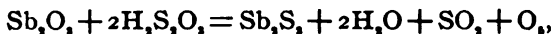
No. of experiment.	Weight of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ added.	Weight of precipitate.
9.....	5 grams.	0.1915
10.....	10 "	0.4041
11.....	15 "	0.5162
12.....	20 "	0.6818

It is evident from these figures that in both sets of experiments the reaction is far from complete and not easily determined. It is, perhaps, quite complex. I noticed in no case the escape of hydrogen sulphide or sulphurous oxide and the gradual change in color during precipitation from very light yellow to bright red suggests that it takes place in two stages. Vortmann (*Ber. d. chem. Ges.*, **22**, 2307) has studied the general problem of decomposition of thiosulphuric acid and states that it breaks up into  $\text{H}_2\text{S}$ ,  $\text{O}$ , and  $\text{SO}_2$ . In presence of certain metals, tetra- and pentathionates seem to be formed. It is certain that no sulphate is formed in the reaction in hand, but the proof of formation of the several thionic acids is difficult because of the incompleteness of the reaction and the presence of the great excess of thiosulphate. In cases of complete reaction, however, Vortmann and Vaubel, also, (*Ber. d. chem. Ges.*, **22**, 2703) have shown that these acids are formed.

I suggest, therefore, this explanation of the present reaction. At the outset there may be, as with borax, a decomposition according to this equation,



then



the oxygen and sulphur dioxide being held, however, to form polythionates.

The gradual change of color can be accounted for by the gradual change of oxide into sulphide of antimony and it seems possible that under certain conditions of concentration and temperature a part of the oxide should remain unchanged, accounting for the results of some of the analysts who have examined the precipitate. In several instances I modified the experiment by mixing warm solutions of the tartar emetic with warm thiosulphate solutions, and then throwing the mixture into a large

volume of cold water the instant a precipitate began to form, to check the reaction. The precipitate which now settled was very light colored instead of red, and appeared to be a mixture of oxide and sulphide. The microscopic appearance of this precipitate is distinctly different from that of the antimony cinnabar.

As explained at the outset some time elapses after mixing cold solutions before a precipitate appears. In the beginning of the interval the solution may be so clear that accurate polarimetric observations are possible. But, contrary to expectations, based on the behavior in other cases recorded, I find the specific rotation of the tartar emetic, in this stage of the reaction, quite unchanged. After precipitation a marked decrease was observed as usual. This is shown in the following table in which the filtrates from the last precipitates referred to were made up to 250 cc. before polarization :

No. of experiment.	Thiosulphate added.	$\alpha_D$ observed.	$\alpha_D$ calculated.
9.....	5 grams.	10.90°	10.89°
10.....	10 "	10.43°	10.46°
11.....	15 "	10.07°	10.24°
12.....	20 "	9.69°	9.93°

In the last column the rotations were calculated on the assumption that antimony is precipitated and Rochelle salt formed according to the last equations. In the eleventh and twelfth experiments the thiosulphate is present in amount much in excess of that necessary to complete precipitation by these reactions, and it is evident that a decomposition of the active molecule has taken place not indicated by the amount of precipitate.

There seems to be a fundamental difference between the reaction with the thiosulphate on the one hand, and those with the borate, carbonate, phosphate, acetate, and tungstate on the other. In the first case we appear to have no breaking up of the complex tartrate until actual precipitation occurs, while in the others the stages are quite distinct. I have shown that in these last reactions acids are liberated which may be readily recognized. It is also true that these acids are practically without action on antimonous oxide, from which it would follow that this substance might remain a long time, possibly in the

hydrated form, in contact with the liberated acids without change. This would not be the case with liberated thiosulphuric acid. If set free in the presence of antimonous oxide, even the dry precipitate, it soon converts it into sulphide. Any cause, therefore, which acts to destroy the equilibrium in the solution of tartrate and thiosulphate must lead to the almost immediate formation of a precipitate.

In many of our most familiar cases of precipitation the formation of the precipitate is so rapid that we are accustomed to look upon it as instantaneous. But by varying the conditions of precipitation it may be shown that even the reaction between barium chloride and sulphuric acid is one which consumes an appreciable interval. In such cases, however, we have no means of knowing what takes place before the precipitate becomes actually visible. It is, doubtless, true that the liquid regarded as supersaturated for  $\text{BaSO}_4$  does not begin to throw this out in solid form until a relatively large number of these molecules combine to produce a particle of a certain size, but at what rate the Ba and  $\text{SO}_4$  ions combine can not be shown.

But in the cases before us we have evidence, first, of the gradual breaking up of the complex potassium antimonyl tartrate and then, also, that a relatively large amount of the antimony may be separated before any of it falls as a precipitate. The stage of precipitation seems to follow as a perfectly distinct and also progressive one. It is hastened, as in other cases of supersaturation, by heat or agitation. One of the reactions shows, also, that a relatively long time is consumed in combination as well as in dissociation. In the case of the mixture containing the tartrate and tungstate we have evidence of the splitting of the first molecule, and then, from the slowly increasing rotation, evidence of the addition of an element from the second to the active part of the first. Both of these phenomena are observed before precipitation appears.

It must be remembered that the several acids shown to be liberated in these experiments are all so-called weak acids, or acids but slightly dissociated in solutions. It is also true, as a test of their electric conductivities shows, that the solutions of tartar emetic are relatively little dissociated (see in this connec-

tion Hugo Haedrich, *Ztschr. phys. Chem.*, 12, 496). There is doubtless, therefore, a close connection between the phenomena outlined above, and others depending on the degree of dissociation of the ions in solution. A study of the behavior of weaker solutions would doubtless lead to interesting results not brought out in the above experiments which were undertaken mainly to show the character and amount of precipitates formed. A discussion of the behavior of dilute solutions will follow.

CHICAGO, December, 1894.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE  
SCHOOL OF APPLIED SCIENCE. XXI.]

## AN EXAMINATION OF THE ATMOSPHERE OF A LARGE MANUFACTURING CITY.<sup>1</sup>

BY CHARLES F. MABERY.

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THE composition of the atmosphere was determined in the latter part of the last century by the classic researches of Priestley, Cavendish, Lavoisier, and others. These investigations were stimulated by Priestley's discovery of oxygen and the discovery of nitrogen by Rutherford. The proportion of nitrogen was first ascertained by Cavendish, and the precise quantitative composition was ascertained by Lavoisier, who repeated the celebrated experiment of Priestley, in which metallic mercury was heated for a long time in a confined volume of air to determine the quantity of gas absorbed and the residual nitrogen. The composition of the atmosphere with reference to the proportion of oxygen and nitrogen has since been frequently determined without showing any appreciable variation. In specimens of air collected from regions widely separated, Morley (*Am. Chem. J.*, 2, 276) determined with the utmost precision the proportion of oxygen and nitrogen without finding any appreciable variation.

The essential constituents of the atmosphere include oxygen, nitrogen, and carbon dioxide in constant proportions, nitrous and nitric acids, sulphurous and sulphuric acids, dust, soot, moisture, ammonia, and certain other constituents in variable

<sup>1</sup>The experimental work of this paper was performed under my direction by Mr. Charles G. Snyder, and it formed the subject of his thesis for the Degree of Bachelor of Science.

proportions depending upon atmospheric conditions and local influences. The allotropic form of oxygen, ozone, is an important constituent of the atmosphere, and probably also hydrogen dioxide.

With a population distributed over large areas, natural conditions are sufficient to keep the atmosphere in a normal and healthful condition for the support of life. Such has been the condition in all civilized countries until within the last thirty years the rapid accumulation of population near manufacturing centers and in cities, and the enormous consumption and incidental waste of coal has introduced important changes at these points. Not only are manufactories and other large establishments dependent for their maintenance upon the consumption of coal, but private habitations, which were formerly heated with wood as fuel with the production of a harmless smoke, now depend almost entirely upon coal. If hard coal is burned the smoke is not objectionable, but the escape of bituminous coal smoke from every household chimney in a densely populated city, together with dense volumes poured forth from large blocks is sufficient to keep the atmosphere in a questionable condition in relation to health, comfort, and the deleterious effects on perishable forms of property. Under occasional conditions of strong winds or rain, followed by clear weather, the city atmosphere is doubtless in a harmless condition; but it can not long remain unpolluted with immense volumes of sooty smoke poured forth from many chimneys.

Abroad, especially in England, the atmosphere of large cities, notably in manufacturing towns, has received considerable attention. Doubtless, on account of the rapid growth of American cities, and probably, also, because of an abundant supply of anthracite coal for cities too far removed from the regions of bituminous coal to render it profitable, the atmosphere of our cities has received little attention. But for cities situated near the soft coal regions, the question of atmospheric pollution has become of too serious moment to be long disregarded.

To understand the nature of smoke pollution it is necessary to refer to the composition of coal and to the products of its combustion under different conditions. Bituminous coal consists

principally of compounds of carbon and hydrogen, or hydrocarbons with smaller proportions of nitrogen and sulphur compounds, and metallic compounds known as the ash when the coal is burned. So far as atmospheric pollution by coal smoke is concerned, the four elements, carbon, hydrogen, sulphur, and nitrogen, are the only constituents of coal that need to be considered.

In the combustion of coal with an adequate supply of air, under such conditions that the chemical reactions involved can be completed within the space allotted to combustion, the ultimate products are carbon dioxide, carbon monoxide, water, sulphurous acid, and ammonia. The less carbon monoxide the smoke contains the more efficient is the combustion; the sulphurous acid is usually converted, at least in part, into sulphuric acid by further oxidation in presence of moisture. It is only rarely, however, that the conditions requisite for complete combustion are maintained. The following features will be recognized as having an important bearing upon the question of complete combustion: (1) A sufficient supply of air; (2) the combustion should not be forced too rapidly; (3) the temperature, especially at the moment of firing, must not be too low; (4) the size, form, and proportions of the space within which the combustion takes place must be suitably adapted. These are the principal points with which complete combustion is concerned, and they are evidently closely connected with the manner of firing and general care of the heating apparatus. In practice, these conditions are far from being realized; with an insufficient supply of air unequally distributed with reference to the fuel, especially with a low temperature, the carbon is only partially burned and the portion not consumed escapes in the form of soot.

The hydrogen burns first, and it has an important influence in maintaining the temperature sufficiently high for complete combustion of the carbon. If the coal contain considerable sulphur it must escape as sulphurous acid, or as sulphuric acid in complete combustion, or (as hydrogen sulphide) in incomplete combustion, and it would seem to be impossible to avoid deleterious effects of these acids in the atmosphere. No doubt sul-

phuric acid should have some effect on such materials as book-bindings and delicate fabrics after collecting in dust during long periods of time, but the effect is greatly increased by the presence of soot, which, as we shall show, absorbs the acid, and when it collects on any surface it occasions a greater accumulation of the acid than should occur in its absence.

The state of the atmosphere in cities where bituminous coal is the principal fuel is dependent upon conditions of combustion in which the chemical reactions are far from complete, with the result that the carbon escapes from the chimney in part as carbon dioxide, in part as carbon monoxide, and in a considerable part as soot. Under such conditions the sulphur is set free as a mixture of sulphuric and sulphurous acids and hydrogen sulphide. The latter is readily shown by its effects on metals, especially on silver, which soon becomes badly discolored on account of the formation of argentic sulphide. The soot ordinarily present in the atmosphere has a greasy consistency, readily recognized by subjecting it to pressure. It consists to a considerable extent of compounds of carbon and hydrogen known as hydrocarbons, which escape from the coal by a process of destructive distillation under conditions somewhat similar to those in the distillation of coal in gas retorts. As mentioned above it carries with it the sulphur acids and ammonia, and it is highly destructive to vegetable life, its action depending probably in part upon the formation on the leaves and stems of a thin layer of tarry substance, which clogs the pores, thus interfering with the process of plant respiration. Sulphuric acid is highly destructive to the forms of organic compounds of which vegetation is composed and in soot it may accumulate to such an extent as to be injurious.

In complete combustion with no escape of soot, even on a very large scale, as in manufactories, it is safe to assert that the natural conditions of the atmosphere may prevent any undesirable effect from the products given off.

During the year 1889 the quantity of coal consumed in Cleveland included 117,157 tons of anthracite and 924,602 tons of bituminous coal. Assuming one per cent. of sulphur in the latter, which is the average composition, 9,246 tons of sulphur



were evolved in the combustion of the soft coal, equivalent to 28,305 tons of sulphuric acid, or nearly eighty tons a day. Without doubt this acid is ultimately neutralized in the atmosphere with the formation of ammonium or sodium salts, but directly it is sent forth it must exist chiefly as the free acid. In the evolution of considerable quantities of sulphur no doubt a portion remains for some time in the atmosphere in the form of sulphurous acid. In the city of Lille, France, as much as two cubic centimeters of sulphurous acid per liter has been found in the atmosphere and the rain water collected contained 0.022 gram per liter.

The ammonia evolved in the combustion of coal is not harmful. Indeed in combination with acids it is a normal constituent of the atmosphere. As one of the ultimate products of the decay of vegetable and animal bodies it is continually set free in this manner and it forms an essential element in the food of plants. The cycle of changes includes the evolution of nitrogen as ammonia from decaying organic bodies and the reabsorption as food by plants from the soils which receive it with the rain. Ordinarily natural conditions are sufficient to complete the transformation of the organic compounds during decay into ammonia in an equal distribution such as exists in the economy of nature. But when accumulation of animal or vegetable organic matter occurs at certain points, as in cities, the oxidizing forces of the atmosphere may not be sufficient to accomplish the vast amount of labor involved in decomposition and purification. On account of the extreme instability of the nitrogenous organic compounds these decompositions take place with great readiness in a limited supply of air but with the evolution of products that are a dangerous pollution in the atmosphere. The evidence of such changes in cities is not far to seek, especially if sanitary regulations are not rigidly enforced. Every stable, imperfect sewer connection, cesspool, sink drain, or offal receptacle readily contributes its share to the atmospheric pollution.

In chemical analysis the nitrogen in such products of decay is evolved as ammonia, and from its source in albumen and allied bodies it is known as albuminoid ammonia. Its presence in water or in the atmosphere may be accurately determined and it

may indicate a dangerous condition since its formation is accompanied with, or perhaps is due to the agency of, organisms which are the means of germinating or spreading disease. As might be expected albuminoid ammonia is usually found in calm weather in the atmosphere of cities.

Ammonia has been mentioned as an ultimate product of decay of nitrogenous organic nature; in the ordinary forms of decay and combustion, ammonia is the chief product, but it is usually attended in combustion with the formation, in small quantities, of nitrous and nitric acids, which may be considered as oxidation products. The extensive knowledge recently acquired, concerning the functions of organized germs, has shown that most forms of decay, and of purification as well, are dependent directly or indirectly upon their influence. Through the agency of the germ known as the niter ferment, for example, ammonia may be converted into nitric acid, and this change is constantly in progress where animal refuse accumulates, as in the vicinity of stables. The magnitude of these changes in nature will be appreciated when it is remembered that most of the niter of commerce has been formed in this manner, either naturally, as in the niter beds in hot countries, or artificially, as in the niter plantations of Sweden. Although nitric acid is the ultimate product of such changes, as an intermediary product, nitrous acid is formed in combustion, and both these acids may be detected in the atmosphere where it is receiving, in large quantities, the products of combustion.

In certain cities, including Cleveland, whose rapid development in wealth and population has been dependent, to a large extent, upon their proximity to immense deposits of cheap fuel, the sooty condition of the atmosphere has rapidly increased within recent years until it has attracted much attention with the feeling that such a condition is not conducive either to personal comfort or to health.

Since, so far as we are informed, a thorough examination of the atmosphere in these cities has not been made, it seemed to us of sufficient interest to undertake a study of the atmosphere of Cleveland with especial reference to the constituents which have been described above, with determinations, so far as practicable, of the quantities present.

As a means of ascertaining the quantity of soot deposited from the atmosphere, and also the amount of sulphuric acid removed from the atmosphere by snow, quantities of snow were collected for examination at the following localities which were assumed to represent an average condition of the city atmosphere,—McHenry St., Erie St., Covington St., and campus of the Case School of Applied Science; and the results, with certain data concerning the collection, are given in the following table:

Location.	Date.	Area.	Weight $H_2O$ from snow melted. Grams.	Weight soot. Gram.
(1) McHenry St.,	Feb. 19,	9 sq. by 1 in. dp.,	3583	0.3117
(2) Erie St.,	Feb. 16,	Col. on roof,	3775	0.1709
(3) Covington St., Newburg,	Feb. 19,		3717	0.4143
(4) C. S. A. S.,	Mar. 22,	$6\frac{1}{2}$ sq. ft. by 1 in. dp.,	3850	0.1611
(5) " "	Mar. 27,	$7\frac{1}{2}$ sq. ft. by $\frac{1}{2}$ in. dp.,	2000	.....

	Weight soot per liter.	Weight $H_2SO_4$ per liter.	Weight $NH_3$ per liter.
(1)	0.0875 gram	0.0152 gram	0.00007 gram
(2)	0.0452 "	0.0063 "	0.00001 "
(3)	0.1113 "	0.0212 "	0.00012 "
(4)	0.0418 "	0.0139 "	0.000003 "
(5)	.....	0.0070 "	.....

These numbers are interesting in showing the large quantity of soot that falls from the atmosphere with the larger amounts collecting at certain points than at others. The quantities of sulphuric acid are large at all points, but nearly three times greater at Covington St., Newburg, near large establishments, than in the more open area near the Case School of Applied Science. The determinations of ammonia indicate an excessive amount at Covington St., and the least at the Case School of Applied Science.

The specific gravity of the water obtained by melting the snow was also determined:

(1).....	1.0010
(2).....	1.0000
(3).....	1.0010
(4).....	1.0005
(5).....	1.0000

These specimens were collected after recent falls before the snow had been contaminated to any considerable extent. The quantity collected on the roof at Erie St. had fallen only a few hours previous to its collection.

On account of the absorptive property of soot it seemed probable that it should retain a considerable quantity of sulphuric acid after it had fallen from the air. For definite proof a quantity of soot was collected on the window sills in the attic of the chemical laboratory, where it had been blown in under the window from the outside. It had probably not been long in collecting. When moistened with water the soot gave a strong acid reaction on test paper, and analysis showed the presence of sulphuric acid.

1.3355 grams of the soot gave 0.00698 gram barium sulphate, equivalent to 1.91 per cent. sulphuric acid.

Another determination of sulphuric acid was made in soot collected in the chimney of a house.

0.4381 gram of this soot gave 0.0459 gram sulphuric acid, which corresponds to 3.17 per cent. sulphuric acid.

Sulphuric acid has invariably been found in testing soot collected in other places.

A noticeable characteristic of a sooty atmosphere and perhaps one of the most important, is the large quantity of soot deposited on the trunks and leaves of trees. In the absence of rain, soot must collect upon the leaves in sufficient quantity to interfere with their natural function of absorbing carbon dioxide. Since it appears that soot and dust absorb sulphuric acid, to a certain extent, from the atmosphere it seemed desirable to ascertain to what extent, if any, this acid collects on the bark of trees. At a point not far removed from manufacturing establishments quantities of bark were scraped from the trunk of a peach, a poplar, a cherry, a hickory, and an oak tree. Probably the kind of tree should not affect the deposition and absorption of acid except perhaps in the degree of roughness of the bark. Nevertheless there are decided differences in the amount of acid from the various sources. The following table gives the results of these determinations :

Variety of trees.	Area.	Total Wt. of bark.	Weight taken for analysis.	Wt. BaSO <sub>4</sub> .	Wt. H <sub>2</sub> SO <sub>4</sub> per sq. foot.	Wt. H <sub>2</sub> SO <sub>4</sub> .
Peach	245.3 sq. in.	17.5750	5.0008	0.0597	0.0251	0.0148
Poplar	280.0 "	3.7534	3.7534	0.0658	0.0277	0.0132
Cherry	200.0 "	2.8886	2.9896	0.0732	0.0308	0.0221
Hickory	400.0 "	3.1333	3.1333	0.0467	0.0196	0.0071
Oak	400.0 "	6.7886	5.0297	0.0352	0.0148	0.0053

In the order of the roughness of the bark the trees examined may be arranged as follows, with the peach as the least rough : peach, poplar, oak, hickory, cherry. Doubtless the deposition of soot containing acid upon the leaves is of even more serious consequence than upon the bark and the effects are clearly apparent on trees situated in the worst portions of a sooty atmosphere. The foliage of such trees exhibits an appearance of decay late in the summer months and the leaves fall early. We did not succeed in collecting specimens of leaves under suitable conditions to determine to what extent acid is retained on their surface.

Some attention has been given to the condition of the trees in such an atmosphere, but more especially with reference to the ravages of parasites that infest trees. In individual instances, no doubt, trees may be totally destroyed in this manner, but it is questionable whether the pernicious effects of a sooty atmosphere are not of more serious consequence on the trees as a whole. The corrosive action of an atmosphere impregnated with soot is daily manifest to the most ordinary observation. I have seen, in the country, nails withdrawn from a shingled roof seventy-five years after the shingles were laid, with the heads apparently unaffected, and the portion between the shingle and the board only slightly rusted away. In the atmosphere of a sooty city, as every one knows, after ten or fifteen years the nails on a roof are nearly consumed.

The effects of such an atmosphere on perishable property, such as certain forms of merchandise, are not so readily discernible, since this material is soon consumed by use. It is in libraries that the effects are most apparent. Fifteen years ago it was demonstrated by the late Professor W. R. Nichols that sulphuric acid is absorbed in bookbindings, and after some time the bindings begin to crumble; he found that the presence of the acid in deteriorated bindings may readily be shown.

The samples of air for examination, were collected at the following points, as fairly representing the different sections of the city.

(1) Campus of Case School of Applied Science, not far from the school buildings and those of Adelbert College. The line of the N. Y., St. Louis & Chicago R. R. is one-eighth of a mile distant toward the south-east.

(2) McHenry St.; closely inhabited, numerous manufactories 700-1,000 feet distant; a line of foundries, steel works, etc., extends three miles along the lake front, one-half a mile distant toward the north from this point. Most of the solid particles of soot fall to the ground within one-fourth to one-half a mile from the source.

(3) Rockwell St.; surrounded by large business blocks. The general condition of the atmosphere is bad on account of the soot, dust from the surrounding streets, and laxity in the enforcement of sanitary regulations.

(4) St. Clair St., near St. Lawrence; many large manufacturing establishments within 500 feet, on the lake shore, all using bituminous coal. When all are in operation, dense volumes of sooty smoke are sent forth into the atmosphere.

(5) West side; on the brow of the hill above the river near Pearl and Detroit Sts. Many locomotives pass below during the hour, and, on the river, tugs pass frequently. When the wind blows from the south-east, this locality is probably one of the worst in the city. The river itself doubtless aids the atmospheric pollution at this point since it is little better than an open sewer with a very sluggish current.

(6) South side, Jefferson St., a residence section with no factories near. In a north-easterly direction is a large ravine containing various kinds of decaying organic matter.

(7) Valley of the Cuyahoga, "Flats"; a very large number of factories of all kinds together with slaughter houses, rendering establishments, etc. Noxious vapors and disagreeable odors from the river invest this entire locality. In clear weather the smoke ascends for the particular benefit of the inhabited districts on the neighboring bluffs. Circulation of the atmosphere is

slow in damp weather and the impure atmosphere remains in the valley.

(8) Genessee Avenue, near Superior St. ; a residence and farming district with no factories nearer than one-fourth of a mile.

(9) Mayfield, three miles outside of the city limits and six miles from the large manufacturing establishments of the city ; a farming section with no barns nearer than one-fourth of a mile of the point where the collection of air was made.

(10) Collinwood, three miles from the city limits, near the Lake Shore Railroad, where locomotives are constantly passing ; numerous barns close together, the nearest 900 feet distant.

Numerous determinations of carbon dioxide at different points in sections of country widely separated have shown no appreciable variation. On the average it is not far from four parts in 10,000 with a variation between three and five-tenths and four and five-tenths parts. Analyses of Cleveland air have shown some variation evidently depending upon the particular conditions at the point where the collection was made :

Locality.	Parts CO <sub>2</sub> per 10,000.
(1).....	3.52
(2).....	3.89
(3).....	4.01
(4).....	3.86
(5).....	4.52
(6).....	4.31
(7).....	4.77
(8).....	3.99
(9).....	3.68

We have attached no particular importance to the determination of carbon dioxide in connection with the principal object of this examination. The following numbers represent the quantity usually present in a city atmosphere :

	Parts in 10,000.
London, England.....	4.39
Glasgow, Scotland.....	5.02
Perth, ".....	4.12
Manchester, England.....	4.42
Cleveland.....	4.42

In determining soot in the atmosphere a measured volume of

air was drawn through a piece of combustion tubing partly filled with ignited asbestos and the carbon was determined by ignition, and absorption of the carbon dioxide as in ordinary combustions. The weights given in the following table are probably somewhat too low, since the soot is doubtless composed, for the most part, of hydrocarbons :

Locality.	Weather.	Wind	Vol. of air at 0° and 76 cm. Liters.	Wt. CO <sub>2</sub> .	Weight soot in 1,000,000 cubic meters.
(1)	Clear	N.	94.0	0.0034 gram	9,875 grams
(2)	"	S. W.	70.2	0.0017 "	6,609 "
(3)	"	N. W.	88.2	0.0051 "	15,773 "
(5)	"	S. W.	92.5	0.0042 "	12,386 "
(5)	"	N. W.	88.7	0.0005 "	1,538 "
(6)	Cloudy	W.	89.3	0.0054 "	16,491 "
(6)	Clear	W.	91.3	0.0027 "	8,065 "
(8)	"	N. W.	94.3	0.0053 "	15,330 "
(8)	"	N. W.	77.9	0.0140 "	39,906 "

A clearer idea may be gained of the quantities of soot given above, if it is understood that 1,000,000 cubic meters is equivalent to the quantity of air contained within a space one mile square and a little more than one and one-fourth feet deep, and that the quantity of carbon, 39.664 grams calculated from analysis of the air collected at Genessee Ave., is equivalent to approximately 8.7 pounds. This very high result has no direct bearing on the quantity of soot in the atmosphere at this point, since it may be attributed to a high wind which filled the air with dust while the experiment was in progress. The air was collected at McHenry St., seven hours after rain had fallen. In certain conditions of the atmosphere frequently observed, there can be no doubt that the quantity of organic dust in suspension is very much larger than is represented by the values given above. The variable proportion of carbonaceous matter in the city air is shown in the duplicate samples collected at the West Side, the South Side, and Genessee Avenue. With the wind blowing from the north-west at the West Side the air is very clear, but in the direction of the south-east, as mentioned above, this section is in the direct line of the smoke from the river valley. Evidently these determinations serve to indicate merely the quantity in suspension in the air examined; but since the soot is rapidly



deposited, these values are, in no sense, a measure of the quantity escaping into the atmosphere.

In determining sulphur in the atmosphere in the form of sulphuric acid, a measured volume of air was drawn through a large U tube containing a solution of sodium hydroxide and broken glass, after passing through ignited asbestos. The alkaline solution was acidified with hydrochloric acid, oxidized with bromine, and the sulphuric acid precipitated with barium chloride. The quantities obtained are given in the following table:

Date.	Locality.	Weather.	Wind.	Velocity of air.
(1) Apr. 9, A. M.	C. S. A. S.	Clear	N. E.	53.9 liters
(2) " 9, P. M.	"	"	Variable	53.9 "
(3) " 13,	"	"	N. E.	6.25 miles 101.5 "
(4) " 19,	McHenry St.	Cloudy	S. W.	3.7 " 27.3 "
(5) June 13,	" "	"	W.	1.5 " 55.7 "
(6) Apr. 23,	Rockwell "	"	N. W.	29.4 "
(7) " 24,	St. Clair "	Hazy	N. W.	3.6 " 28.8 "
(8) " 27,	Riv. Val.	Clear	S. E.	5 " 27.6 "
(9) June 29,	" "	Cloudy	N.-S.	5.5 " 47.8 "
(10) Apr. 30,	W. Side	Clear	S. W.	1.5 " 28.3 "
(11) May 1,	S. Side	Cloudy	W.	4.5-18.3 " 28.0 "
(12) " 7,	Genessee Ave.	"	N. W.	8.7-2.5 " 28.6 "
(13) " 15,	Collinwood	Hazy	N. E.	44.2 "
(14) June 26,	Mayfield	Clear	S. W.	7.5 " 39.8 "

Locality.	Weight BaSO <sub>4</sub> .	Grams H <sub>2</sub> SO <sub>4</sub> in 1,000,000 cu. met.
(1) .....	0.0030	23414
(2) .....	0.0028	21859
(3) .....	0.0053	20178
(4) .....	0.0027	42156
(5) .....	0.0022	16615
(6) .....	0.0033	47801
(7) .....	0.0011	16142
(8) .....	0.0033	50629
(9) .....	0.0033	29014
(10) .....	0.0057	56828
(11) .....	0.0042	63289
(12) .....	0.0023	33989
(13) .....	0.0000	.....
(14) .....	0.0007	7392

The variation in the quantity of sulphuric acid in the atmosphere is shown in the duplicate determinations at McHenry St., and the river valley, made at different dates. A negative result

at Collinwood is, perhaps, what might be expected in country air under certain conditions. And yet it seems that it was possible for sulphuric acid to be carried as far as Mayfield. It would be interesting to examine the atmosphere at different distances outside the city to ascertain how far the influence of the city air extends.

The following weights in grams of sulphuric acid in 1,000,000 cubic meters, have been found in the atmosphere of cities in England:

London .....	1669.935
Didsbury.....	1337.844
Blackpool.....	474.413
Buxton.....	1494.400
Manchester .....	2443.738

As already explained, sulphur sent forth into the atmosphere from the combustion of coal may escape complete oxidation and appear in part as hydrogen sulphide and in part as sulphurous acid. In testing for sulphurous acid in the atmosphere near the Case School of Applied Science, a measured volume of air was drawn through the alkaline solution for absorption, and in one portion the sulphuric acid was precipitated with barium chloride. The weight of barium sulphate corresponded to 20,276.36 grams of sulphuric acid in 1,000,000 cubic meters. To the remaining portion of the solution used for absorption bromine was added for oxidation, and the solution precipitated with barium chloride. The difference in weights corresponded to 33,033.1 grams of sulphuric acid in 1,000,000 cubic meters. In further confirmation of the presence of both sulphurous and sulphuric acids, another determination was made on the "Flats," near the Central viaduct, on an exceptionally clear day. In eighty-six liters of air aspirated, the total weight of barium sulphate, after oxidation, corresponded to 0.0058 gram barium sulphate, and the weight of barium sulphate before oxidation was equivalent to 0.0028 gram barium sulphate, the difference, 0.0031, representing the sulphurous acid in the total volume of air aspirated. The quantity of sulphuric acid present was, therefore, represented by 11,851 grams, and the sulphurous acid by 12,512.6 grams in 1,000,000 cubic meters.

In the atmosphere of other cities, notably in Manchester,

England, and Lille, France, sulphurous acid has been determined, and it is probable that it may always be detected in the atmosphere where it receives large quantities of smoke from the combustion of coal.

The presence of ammonia as a normal constituent of the atmosphere has already been mentioned, and under ordinary conditions it does not collect in sufficient quantity to be injurious. Nevertheless, it seemed of interest to ascertain to what extent this constituent collects in an atmosphere contaminated with soot. In collecting ammonia, a definite volume of air was drawn through a dilute solution of hydrochloric acid, and both free and albuminoid ammonia were determined by the methods ordinarily employed in water analysis. After the free ammonia was distilled the residual solution was oxidized with alkaline permanganate until there was no further evolution of ammonia, and both sets of distillates nesslerized. The following tables give the quantity of free and albuminoid ammonia from the quantity of air aspirated in each locality and the state of the weather.

	Date.	Locality.	Weather.	Wind Direc.	Wind Veloc.	Volume of air in liters.
(1)	Apr. 6,	C. S. A. S.	Clear	N. W.	9 m.	48.024
(2)	" 6,	"	Cloudy	"	6 "	46.071
(3)	" 19,	McHenry St.	"	S. W.	4 "	20.391
(4)	June 13,	" "	"	W.	1.5 "	6.941
(5)	Apr. 23,	Rockwell "	"	N. W.	4 "	22.334
(6)	" 24,	St. Clair "	Hazy	N. W.-W.	2 "	22.163
(7)	June 20,	" " "	Clear	N.	"	6.963
(8)	Apr. 30,	West Side	"	S. W.	18 "	21.282
(9)	" 27,	" "	"	N. W.	1 "	7.054
(10)	May 1,	South Side	Cloudy	W.	1 "	20.971
(11)	June 22,	" "	Clear	W.	0.5 "	7.092
(12)	May 7,	Genessee Ave.	Cloudy	N. W.-S. W.	8.7-25m	6.622
(13)	June 21,	" "	Clear	N. W.	1 m.	6.829
(14)	" 26,	Mayfield	"	S.	7.5 "	6.781
(15)	" 29,	River Valley	"	N. W.	6.5 "	6.862

	Total free NH <sub>3</sub> .	Total Albuminoid NH <sub>3</sub> .	Free NH <sub>3</sub> in 1,000,000 cu. met.	Albuminoid NH <sub>3</sub> in 1,000,000 cu. met.
(1)	0.0000051	0.0000071	106.10 grams	147.84 grams
(2)	0.00000490	0.0000045	106.35 "	97.67 "
(3)	0.00002180	0.0000113	1070.20 "	557.50 "
(4)	0.00000210	0.0000021	302.50 "	298.90 "
(5)	0.00000780	0.0000035	357.20 "	158.90 "
(6)	0.00002330	0.0000051	1051.10 "	230.10 "

	Total free $\text{NH}_3$ .	Total Albuminoid $\text{NH}_3$ .	Free $\text{NH}_3$ in 1,000,000 cu. met.	Albuminoid $\text{NH}_3$ in 1,000,000 cu. met.
(7)	0.0000014	0.0000023	198.7 "	329.1 grams.
(8)	0.0000082	0.0000037	385.5 "	173.8 "
(9)	0.0000059	0.0000030	836.9 "	430.9 "
(10)	0.0000169	0.0000043	806.4 "	202.5 "
(11)	0.0000015	0.0000007	214.5 "	100.6 "
(12)	0.0000086	0.0000031	1373.0 "	489.5 "
(13)	0.0000030	0.0000034	440.6 "	492.0 "
(14)	0.0000035	0.0000019	510.2 "	282.8 "
(15)	0.0000054	0.0000010	787.7 "	150.1 "

We have found on record but few determinations of free and albuminoid ammonia, but similar determinations have been made in certain cities abroad, the results of which afford an interesting comparison with those we have obtained.

	Grams free $\text{NH}_3$ in 1,000,000 cu. met.	Grams albuminoid $\text{NH}_3$ in 1,000,000 cu. met.
London.....	61.286	150.919
Glaagow.....	78.196	304.974
Innellan.....	52.281	137.832

These numbers represent much smaller quantities of albuminoid ammonia, and still smaller quantities of free ammonia than appear in the results of our determinations.

It has long been known that nitrous acid and nitric acid are contained in the products of combustion from fuels containing nitrogen as most fuels do. These acids represent a more advanced stage of oxidation than ammonia; they are derived to a certain extent, it may be, from the oxidation of atmospheric nitrogen; and they may also be detected in the products of respiration. Ammonium nitrate may be found in dew and it seems to be present in larger quantities in spring than in summer and more at night than during the day. These acids are, therefore, normal constituents of the atmosphere under natural conditions, and the minute quantities usually present can not be considered harmful.

In testing for nitric acid we used as an indicator phenolsulphonic acid prepared by dissolving phenol in concentrated sulphuric acid and for comparison, a solution of potassium nitrate in which one cc. contained 0.000001 gram nitrogen. For nitrous acid, sulphanilic acid and naphthylamine hydrochloride were used as indicators with a solution of sodium nitrite, in which one cc. contained 0.000001 gram nitrogen as a means of com-

parison. A measured volume of air was drawn through a solution of sodium hydroxide prepared from metallic sodium, and definite quantities of this solution were used in each determination.

The following tables give the quantities of nitrous and nitric acids found in experiments conducted at different localities with other data of the collection :

## NITROUS ACID.

Date.	Place.	Weather, &c.	Grams $\text{HNO}_2$ in 1,000,000 cub. met.
Apr. 17,	C. S. A. S.	Clear W. N. E.....	6.767
May 11,	"	" W. N. W.....	0.000
July 2,	"	Cloudy Calm.....	6.955
April 19,	McHenry St.	" W. S. W.....	119.277
June 30,	" "	Clear W. N. W.....	73.976
April 23,	Rockwell "	Cloudy Damp.....	152.785
June 16,	" "	Clear W. N. W.....	8.856
Apr. 24,	St. Clair "	" W. N. W.....	126.614
June 20,	" "	" W. N.....	135.500
June 29,	River Valley	Cloudy W. N. W.....	0.607
May 4,	West Side	Clear W. N. W.....	15.206
June 27,	"	" W. N. W.....	19.945
June 22,	South Side	" W. W.....	1.239
May 7,	Genessee Ave.	" W. N. W.....	5.833
June 21,	" "	" W. N. W.....	7.228
May 15,	Collinwood	Cloudy Calm.....	4.564

## NITRIC ACID.

Date.	Place.	Grams $\text{HNO}_3$ per 1,000,000 cub. met.
April 17,	C. S. A. S. ....	674.5
May 11,	" .....	560.0
April 19,	McHenry St.....	703.8
June 13,	" " .....	54.99
April 24,	St. Clair St.....	520.5
June 20,	" " .....	144.0
April 27,	River Valley.....	704.0
June 27,	" " .....	68.8
April 30,	West Side .....	1063.6
May 4,	" " .....	367.6
June 27,	" " .....	66.9
May 1,	South Side.....	61.8
June 22,	" " .....	153.8
May 7,	Genessee Avenue .....	333.6
June 21,	" " .....	129.4
May 15,	Collinwood .....	424.0
June 16,	Rockwell St.....	544.8
June 26,	Mayfield .....	44.5

The variation in the proportion of both nitrous and nitric acids under different conditions is very marked, as shown in the samples of air collected in the river valley, the West Side, and McHenry St.

From the results of this examination it is evident that a city atmosphere, contaminated by the universal consumption of bituminous coal, where no efforts are made to prevent the escape of soot, soon reaches a stage in which it is destructive to property and not conducive to health. In this respect the atmosphere of Cleveland is, doubtless, no worse than that of other cities, and, perhaps, in a better condition than some that use the same fuel. Under the usual conditions of life in cities, sanitary regulations require careful attention and constant supervision.

### A NEW FORM OF WATER-OVEN AND STILL.<sup>1</sup>

BY LEWIS WILLIAM HOFFMANN AND ROBERT W. HOCHSTETTER.

Received November 8, 1894.

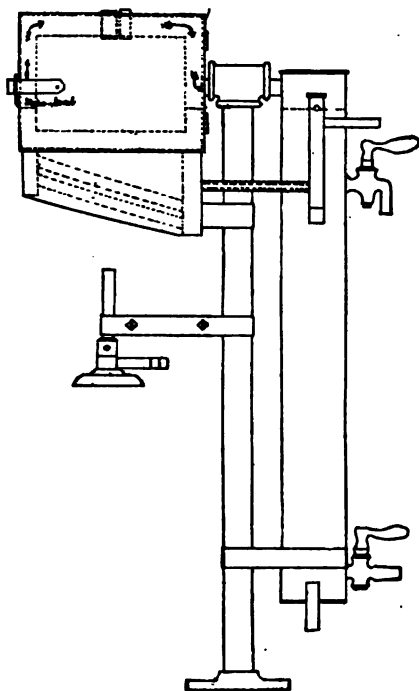
In the use of the ordinary form of water-oven we have been impressed with the fact that there are several disadvantages connected with that form of this apparatus. For instance, there is the necessity for refilling it from time to time, with the consequent fall in temperature and loss of time; there is the waste of steam which might be condensed to the always-useful distilled water, and we have had trouble in obtaining a constant temperature of 100° C. To obviate these difficulties we have devised the combined oven and still which we describe here—a piece of apparatus that has an automatic feed, a worm for condensing the steam and an arrangement of the heating surface so as to provide for perfect circulation and quiet boiling, with steady and abundant generation of steam.

The combination of still and oven is not new, for in the April, 1892, number of the *Journal of Analytical and Applied Chemistry*, Herbert M. Hill describes such a piece of apparatus in use in the Buffalo University laboratory. Except for the combination it bears little resemblance to our apparatus.

In our form of apparatus, the heating surface consists largely of a series of pipes, connected with water boxes at each end.

<sup>1</sup> Read before the Cincinnati Section, October 15, 1894.

These pipes, through which the water circulates, are inclined so as to afford an easy ascent for the steam generated in them, as the result of the heat applied to their outer surface. The source of heat is an ordinary Bunsen burner, used with a wing-tip, so as to spread the flame over the surface of the pipes. The pipes are of small diameter so as to afford a large heating surface in proportion to the amount of water passing through them.



The steam is carried off at a point about half-way up the side of the oven and passed through a block-tin condenser. To reach the condenser the steam must pass over the top of the drying-chamber, as the water-level in the oven is kept about one-fourth of the distance

between the top and bottom, thus acting as a lute and compelling the steam to pass up and over in order to escape. The water used in cooling the worm also serves as feed-water for the oven, and as it passes from the bottom to the top of the condenser, absorbs so much heat as to enter the water-box already heated almost to the boiling-point. The feed-pipe is so small that the circulation between condenser and oven is slow but constant. A stop-cock is provided at the top of the condenser, for drawing off hot water if desired. A small hole in the door and another in the top provide for ventilation of the drying chamber. Sedimentation takes place in the condenser so that almost clear water goes into the heating-pipes.

To the factory chemist, having always a plentiful supply of condensed steam at his disposal, this piece of apparatus may not seem of much value, but to the analyst, a combination of

still and water-oven means a saving of time, trouble, and, in some cases, expense.

The advantage derived from the arrangement of pipes for receiving heat, (an idea borrowed from the Babcock-Wilcox boiler,) may be conceived from the statement that while in the oven which we have, the heating surface measures 82.8 square inches, but seven square inches of this area is the bottom of the oven, the rest being made up by the pipes and the sides of the water-boxes at each end.

Now as to the work done by the apparatus. The oven which we have in our laboratory will get up steam in four minutes after the flame is lighted, and at the expiration of six and two-tenths minutes will be delivering distilled water. This is with a Bunsen burner consuming three cubic feet of gas per hour. With a burner consuming twice as much gas, one and three-tenths minutes is gained in steaming, and two and two-tenths minutes in delivering water.

The still delivers water at the rate of two and one-fourth quarts per hour or thirteen and one-half gallons in twenty-four hours—this with a three-foot gas-burner. A patent automatic still which we have hitherto been using, consumes six cubic feet of gas per hour, and delivers two quarts of water an hour, or twelve gallons in twenty-four hours, although the claim made for it by the makers is fifteen gallons in twenty-four hours.

The temperature in the drying chamber of our form of apparatus ranges from  $98^{\circ}$  to  $101^{\circ}$  C., so that it may be said to average  $100^{\circ}$ .

The advantages claimed for our form of apparatus are as follows:

A constant temperature of  $100^{\circ}$ , which in our experience, can not be obtained with the ordinary form of oven.

A large yield of distilled water, with a small expenditure of heating material, and practically no cost, as the water-oven is nearly always in use in a working laboratory.

Hot water always at command.

Small space occupied by both oven and still.

General convenience of arrangement.

MT. AUBURN, CINCINNATI,  
November, 1894.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE  
UNIVERSITY OF MICHIGAN.]

## THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

R. D. CAMPBELL AND W. H. ANDREWS.

Received December 24, 1894.

SINCE publishing his former method for the determination of nickel in nickel-steel (This JOURNAL, 16, 96), the author has been endeavoring to perfect another method which should be an improvement over the first one. Such accurate results have been obtained in so short a time by this method that it is thought desirable to give the details of manipulation.

Place a one gram sample of nickel-steel in an Erlenmeyer flask of about one-half liter capacity. Add twenty-five cc. of nitric acid (1.20) and boil until dissolved and nitric oxide is boiled out of the flask. Meanwhile, dissolve thirteen grams of sodium pyrophosphate in seventy-five cc. of warm water. This solution must not be boiled as the pyrophosphate is thereby converted to the orthophosphate.

After complete solution, filter the sodium pyrophosphate and add it to the cooled solution of the steel. This will give a heavy, white precipitate of ferric pyrophosphate. Add, a little at a time, with constant agitation, a clear twenty per cent. solution of sodium carbonate until the precipitate of ferric pyrophosphate just dissolves and the solution attains a dull, olive-green color.

An excess of sodium carbonate must be carefully avoided, as the subsequent precipitation of nickel will not be complete if this is not done. With an excess of the carbonate the solution turns red, so that color may be used as a guide to the required amount. For a one gram sample, fifty to fifty-five cc. of twenty per cent. sodium carbonate is usually sufficient.

After redissolving with sodium carbonate, filter through asbestos, receiving the solution in a one-half liter Erlenmeyer flask; wash the filter with water sufficient to rinse out the original flask and to insure complete transference of the solution. Now add to the solution two grams of potassium xanthate freshly dissolved in twenty to twenty-five cc. of water. Stopper the flask and shake at frequent intervals for ten minutes. The nickel will be

completely precipitated as xanthate, together with any copper the steel may contain, but perfectly free from manganese and almost free from iron. Filter as rapidly as possible through asbestos, using a pump, and wash the brick-red nickelous xanthate four or five times with freshly prepared one per cent. potassium xanthate.

The solution of potassium xanthate used for precipitating, as well as that used for washing, should be prepared by adding to the desired amount of salt sufficient water for solution, but should not be allowed to stand longer than fifteen or twenty minutes before using as it slowly decomposes. The dry salt is stable.

Dissolve the washed precipitate off the filter by allowing twenty cc. of freshly diluted fuming nitric acid to fall little at a time on it. The dilute fuming nitric acid should be prepared just before using by pouring ten cc. of water into ten cc. of fuming nitric acid. Catch the solution of the xanthate precipitate in a small Erlenmeyer flask. Wash the filter two or three times with hot water, then pass through five cc. of dilute sulphuric acid (2:3) and wash this out with more hot water. Boil the solution in the flask rapidly until the nitric acid is completely expelled and sulphuric anhydride fumes begin to rise. Cool, add twenty to twenty-five cc. of water, heat nearly to boiling, and, when all is in solution, pass in hydrogen sulphide for two or three minutes. Allow to stand until the cupric sulphide has settled. Filter and wash with hot water containing a little hydrogen sulphide.

Boil the filtrate, containing the nickel and a very small amount of iron, until hydrogen sulphide is expelled, add a few drops of hydrogen peroxide, or a few milligrams of sodium peroxide to oxidize the iron, and boil, then precipitate the iron with a very slight excess of ammonium hydroxide. Boil, filter, and wash once or twice with hot water. Dissolve the small precipitate of ferric hydroxide off the filter with five cc. of dilute sulphuric acid (2:3) and reprecipitate with a slight excess of ammonium hydroxide. Boil and filter into the original filtrate. This solution will contain all the nickel free from iron, manganese, and copper. The nickel may be determined in either of the following ways:

1. *Electrolytically*.—Place the united filtrates from the ferric hydroxide in a platinum dish having a capacity of about 200 cc., add thirty cc. of a ten per cent. solution of disodium hydrogen phosphate, then twenty-five cc. of strong ammonium hydroxide. The solution should have a bulk of about 175 cc. Electrolyze for twelve hours with a current of 0.14 amperes per 100 sq. cm. area of the dish, having the electrodes about one-half cm. apart.

The precipitate of nickel obtained in this way is perfectly clear and bright, hardly to be distinguished from the platinum on which it is deposited.

Wash the precipitated nickel with warm water then with alcohol. Dry and weigh as usual. For accurate work it is more satisfactory to use a second platinum dish washed and dried like the first, as a counterpoise.

2. *Volumetrically*.—Place the united filtrates from the ferric hydroxide in a medium sized Erlenmeyer flask and cool until cold. The solution should have just enough free ammonia to give a slight but distinct odor; if this is not present at this stage, add a few drops of ammonium hydroxide. Add five cc. silver nitrate indicator (made by dissolving five-tenths gram silver nitrate in 1,000 cc. of water). Add five cc. of a two per cent. solution of potassium iodide, which give the solution an opalescence due to the presence of silver iodide in suspension.

Run in standard potassium cyanide (one cc. = 0.001 gram nickel) until the solution becomes clear and bright. The titration depends upon the fact that so long as there is any nickel uncombined with potassium cyanide in the form of the double cyanide, the silver iodide will remain undissolved, but as soon as the nickel has all been changed the silver iodide dissolves forming potassium silver cyanide and the solution becomes perfectly clear.

Subtracting a correction necessary for the titration of the indicator from the total amount of potassium cyanide used, gives the amount necessary for the nickel.

*Standard Solutions Required*.—Standard nickel solution: This can be most easily prepared from pure nickel wire. The commercially pure nickel wire usually contains 98.5–99.5 per cent.

nickel. If this wire is used for making the standard solution, take such a weight as will represent one gram of pure nickel, dissolve in a No. 3 beaker with twenty-five cc. nitric acid (1.42) and evaporate just to dryness on the water-bath. Moisten with a few drops of nitric acid, add about twenty-five cc. of water, and heat to solution. When the nickel is dissolved, dilute to fifty or sixty cc., add six grams of sodium acetate dissolved in a little water, heat nearly to boiling until the ferric basic acetate separates. Filter, and wash thoroughly with hot water. Add five cc. of sulphuric acid to the solution, transfer to a graduated liter flask, cool, and dilute to 1,000 cc.

*Standard Potassium Cyanide.*—Dissolve four and five-tenths grams of potassium cyanide in water and dilute to 1,000 cc. This must be standardized against the standard nickel solution.

Run in from a burette twenty-five to thirty cc. of the nickel solution into a medium sized Erlenmeyer flask, dilute with water to about 100 cc., add ten cc. of dilute sulphuric acid (2:3); then add ammonium hydroxide carefully until a slight but distinct odor of ammonia is perceptible. Add five cc. of silver nitrate indicator, five cc. of two per cent. potassium iodide and titrate with potassium cyanide until the solution brightens. Correction for the indicator is found by proceeding exactly as above, except that the standard nickel solution is omitted.

The potassium cyanide is quite stable, weakening, however, gradually on standing. The deterioration amounted from five-hundredths to one-tenth cc. in twenty-five cc. during one week.

In order to test fairly the accuracy of the recovery, the varying amounts of pure nickel wire were weighed and dissolved by my private assistant, who turned them over to Mr. Andrews as strictly unknown samples. Weighed amounts of iron wire were then added and the solution proceeded with as if it were an ordinary sample of steel.

Two hours is sufficient time to get the solution ready for electrolysis or for titration.

The following table will show the accuracy of the results obtained, where the amount of nickel present was strictly unknown to the operator until the analysis was completed:

Iron added. Grams.	Nickel taken. Gram.	Nickel recovered. Gram.	Gain and loss.		Method.
			+	-	
0.2105	0.08892	0.08910	+ 0.00018		Electrolytically.
1.0000	0.03430	0.03435	+ 0.00005		"
1.0041	0.05298	0.05345	+ 0.00047		"
1.0043	0.10824	0.10825	+ 0.00001		"
2.0043	0.02690	0.02740	+ 0.00050		"
1.0010	0.00100	0.00089	- 0.00011		Volumetrically.
1.0086	0.06578	0.06532	- 0.00046		"
1.0066	0.07582	0.07583	+ 0.00001		"
1.0057	0.08017	0.08050	+ 0.00033		"
1.0071	0.09389	0.09381	- 0.00008		"

ANN ARBOR, MICHIGAN,  
December 18, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE  
POLYTECHNIC INSTITUTE. VI.]

## THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.<sup>1</sup>

BY W. A. NOYES AND J. S. ROYBE.

Received January 3, 1895.

IN a previous paper<sup>2</sup> one of us, with Mr. E. D. Frohman, showed that in the reduction of molybdic solutions by means of Jones' reductor, the molybdenum is reduced to a form corresponding to the oxide  $\text{Mo}_2\text{O}_3$ . We also showed that the reduced solution is very easily oxidized by exposure to the air, and we were led to believe this would account for the difference between the theoretical factor for the calculation of the phosphorus equivalent of a permanganate solution from its iron equivalent, and the empirical factor as given by Dudley and Pease.<sup>3</sup>

In a private communication, however, Dr. Dudley has very kindly called our attention to the fact that he obtained the same results when following the directions for reduction given in our paper as when following the method which he had previously used. As the difference between his results and ours corresponded to only three-tenths or four-tenths cc. of the permanganate solution used, and the results obtained by Mr. Frohman

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

<sup>2</sup> This JOURNAL, 16, 553.

<sup>3</sup> This JOURNAL, 16, 230.

were not sufficiently accordant to establish the point in question, it became necessary to repeat that part of the work. Accordingly, the following series of determinations was made, following, as closely as possible, the directions given by Dudley and Pease.<sup>1</sup> The results are given in per cents., on the basis of one gram of steel.<sup>2</sup>

	Phosphorus present.	Phosphorus found.	
		By theoretical factor.	By factor of Dudley and Pease.
Steel No. 1.....	0.040	0.040	0.045
“ “ 1.....	0.040	0.0354	0.0397
“ “ 2.....	0.053	0.0525	0.059
“ “ 2.....	0.053	0.0525	0.059
“ “ 3.....	0.032	0.0264	0.0296
5 grams cryst. $\text{FeSO}_4 + 0.0011$ gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.010	0.0035	0.0039
5 grams cryst. $\text{FeSO}_4 + 0.0130$ gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.113	0.127	.....
5 grams cryst. $\text{FeSO}_4 + 0.0097$ gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.084	0.091	.....
5 grams cryst. $\text{FeSO}_4 + 0.0109$ gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.094	0.106	.....
1 gram steel No. 3 + 0.0068 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.091	0.097	.....
1 gram steel No. 3 + 0.0026 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.055	0.054	0.0061

The first result is evidently wrong for some unknown reason. Omitting this, the results with steels Nos. 1 and 3 show conclusively that the factor of Dudley and Pease is correct for those steels and the statement of our first paper was erroneous. As regards steel No. 2 the case is different. Dudley and Pease explain the higher results obtained with this steel as due to arsenic which it contains. The results of the last determination in the table, and, still more, the results obtained by another method and given below, lead us to believe that this is not the case, but that for a steel containing 0.055 of phosphorus the theoretical factor gives very nearly correct results.

From the examination of the table as a whole it becomes apparent, at once, that, while the factor given by Dudley and Pease gives results nearly or quite correct for steels containing 0.03 to

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

<sup>2</sup> This set of determinations was made by W. A. Noyes.

0.04 per cent. of phosphorus, it fails entirely so soon as the amount present is either above or below these limits. The reason is, we believe, apparent. When the amount of phosphorus is less than 0.05 per cent., a part of it escapes precipitation, and hence, a larger factor than the theoretical is required. When the amount of phosphorus is as great as 0.08 per cent. or more, however, the yellow precipitate probably carries down with it at 55° C., some free molybdic anhydride, and even the theoretical factor gives too high results. If we retain the method in its present form, therefore, it will be necessary to use several different empirical factors, or to apply a correction varying with the amount of phosphorus present in the steel under examination. We believe such a course is open to very serious objection and that it should be avoided, if possible. The use of a variable correction implies that the yellow precipitate is not a pure chemical compound, but that it has a variable composition dependent on the amount of phosphorus present. If we admit this, it is evident that the method is not a suitable one on which to base an accurate determination, for a compound or mixture of variable composition is liable to be seriously affected by even slight changes in manipulation, changes which are sure to occur in different hands and different laboratories.

These considerations led us to endeavor to modify the method in such a manner as to secure, if possible, a practically complete precipitation of very small amounts of phosphorous and also to secure the precipitation in the form of a compound of definite composition and independent of the amount of phosphorus present. The considerations which have guided us in the study are as follows: first, the precipitation would be more rapid in a more concentrated solution; second, the precipitation must be at a lower temperature than 55° to prevent the contamination of the precipitate with molybdic anhydride; third, the precipitate is formed more rapidly in a more nearly neutral solution; and fourth, the presence of ammonium nitrate hastens the formation of the precipitate, probably because ammonium enters into its composition.

Without going into the details of unsuccessful experiments, we will give the method which we have found most satisfactory.

We give details for reagents and apparatus, though most of these details are a repetition of those given by Dudley and Pease.

#### REAGENTS AND APPARATUS.

*Nitric Acid.*—One part of concentrated acid (1.42) to two parts of water by volume. This gives an acid of sp. gr. 1.18.

*Oxidizing Permanganate Solution.*—Twelve and one-half grams of potassium permanganate in one liter of water.

*Ferrous Sulphate.*—The crystallized non-effloresced salt, *free from phosphorus*.

*Ammonia.*—Concentrated, sp. gr. 0.90; and dilute, sp. gr. 0.96.

*Molybdic Solution.*—Dissolve 100 grams of molybdic anhydride in 400 cc. of ammonia (0.96), filter and pour the solution slowly, with constant stirring, into 1,000 cc. of nitric acid (1.20). Warm to 45°, add one cc. of a ten per cent. solution of crystallized sodium phosphate, stir vigorously, and allow to stand in a warm place over night before using. The addition of the sodium phosphate was suggested by Dr. Dudley and has the two-fold object of precipitating anything liable to contaminate the yellow precipitate and of leaving the solution saturated with the compound which is to be precipitated by it. Our experience leads us to think that the solution keeps better in the dark. It is always safer to filter it immediately before it is used and the solution must, of course, be absolutely clear. If pure, it will be almost or quite colorless, but we have found that a somewhat yellow solution prepared as above, gave us results nearly or quite identical with those obtained with a colorless solution.

*Acid Ammonium Sulphate.*—To one half liter of water add twenty-seven and one-half cc. of ammonia (0.96) and twenty-four cc. of concentrated sulphuric acid and make up to one liter.

*Potassium Permanganate for Titration.*—Dissolve four grams of potassium permanganate in two liters of water, heat nearly to boiling for an hour, allow to settle over night, and filter with the pump, using an asbestos filter prepared after the manner of Gooch on a small perforated porcelain plate placed in the bottom of a large funnel. Use very great care that the solution does not come in contact with india-rubber or any kind of organic matter and keep in a clean glass-stoppered bottle, free from



manganese oxides. We find that a solution prepared in this manner keeps perfectly and is not affected by the light.

We prefer to standardize with freshly crystallized and thoroughly air-dried ammonium oxalate dissolved in water with the addition of a little dilute sulphuric acid (instead of considerable concentrated acid as advised by Fresenius) and with ferrous ammonium sulphate freshly crystallized in small crystals from a slightly acid solution, the crystals being thoroughly washed and quickly air-dried in a thin layer, using the factors  $\frac{1}{112}$  and  $\frac{1}{142}$  respectively to calculate the iron equivalent<sup>1</sup>. The phosphorus equivalent is obtained by multiplying the iron equivalent by  $\frac{31}{56 \times 98} = 0.01538$ .

*Jones' Reductor.*—A piece of moderately heavy glass tubing thirty-five cm. long and having an internal diameter of about two cm., is drawn out at one end to pass through the stopper of a filtering flask. In the bottom of the tube is placed a small perforated porcelain plate and on this is prepared an asbestos filter, practically a Gooch filter. This filter should offer enough resistance so that a reduction will occupy two or three minutes. The tube is nearly filled with powdered zinc, which is then washed with dilute sulphuric acid (1:20 by volume). Blank determinations are made as follows: To 180 cc. of water, add twelve cc. of ammonia (0.96) and ten cc. concentrated sulphuric acid. Pass the solution through the reductor and follow with 200 cc. of water, *taking care that no air passes through the reductor*. It is easily shown, qualitatively, that hydrogen peroxide is formed by passing air and water alternately through the reductor. After standing, even for a few minutes, the reductor should be rinsed with dilute sulphuric acid before use. Blank determinations should be made frequently and the amount of

<sup>1</sup> The method given by Dudley and Pease (This JOURNAL, 15, 521.) has given me practically identical results with the above methods, also piano wire, considering it as pure iron, the impurities in iron, some of them, requiring more permanganate than iron itself. The following results were obtained:

Iron wire (Fresenius' method).....	0.003199
Ammonium oxalate.....	0.003209
Ferrous ammonium sulphate.....	0.003209
Dudley's steel.....	0.003179
" " .....	0.003205
" " .....	0.003208

W. A. NOYES.

permanganate required should be subtracted from that found in an analysis. The blanks should not take more than two-tenths to three-tenths cc. of permanganate. Ours are usually less than two-tenths cc. We do not think it advisable to use the same reductor for both iron and molybdenum solutions.

#### ANALYTICAL PROCESS.

Weigh two grams of steel<sup>1</sup> to an accuracy of two mgms., put it in a 500 cc. (16 oz.) flask, add fifty cc. of nitric acid (1.18), and warm, only gently, till solution is complete, (our experience leads us to think some phosphorus may escape if the gases in the flask become colorless before solution is complete); then boil for one minute, add ten cc. of the permanganate solution (one and one-fourth per cent.), boil till the pink color disappears, add ferrous sulphate carefully, with shaking, till the solution clears, cool to about 50°, add eight cc. ammonia (0.90), insert the stopper, and shake till any precipitate which forms redissolves; cool or warm till the solution is as many degrees above or below 60° as the molybdic solution is below or above 27°, add sixty cc. of molybdic solution, insert the rubber stopper, and shake by hand or with a machine for five minutes; allow to settle for five minutes, filter through a nine cm. filter of rather fine texture, wash with the acid ammonium sulphate solution, putting five or ten cc. at a time into the precipitation flask and pouring from that all around the upper edge of the filter. The filtrate and washings must be absolutely clear. Wash till five cc. of the washings give no brown color with a few drops of dilute hydrogen sulphide water. Pour over the precipitate twelve cc. of ammonia (0.96) diluted to twenty-five cc., allow the solution to run into the precipitation flask, wash with 100 cc. of water, add eighty cc. more of water and ten cc. of concentrated sulphuric acid, pass the solution through the reductor and follow it with 200 cc. of water, *taking care that no air passes through the reductor during reduction or washing.* Titrate the solution, *at once, in the reductor flask.*

With steels high in phosphorus, the ammoniacal solution of the yellow precipitate may be made up to a known volume and an aliquot part taken for reduction.

<sup>1</sup> Dr. Dudley suggested the use of two grams of steel.

For cast iron low in phosphorus, the method may be carried out exactly as given for steel. The method may also be used without modification other than the use of a larger amount of ammonia for solution of the yellow precipitate and the use of an aliquot part of the solution for reduction, for cast iron high in phosphorus. We prefer, however, in that case, to use one gram of the iron, dissolve, oxidize, clear, and neutralize as usual, using twelve cc. of ammonia. Then the solution is made up to 150 or 250 cc. and ten cc., or more, taken, enough water added to make fifty cc., the solution warmed to 60° and sixty cc. of molybdic solution added. The remainder of the process is as above for steel. The residues insoluble in nitric acid may require examination as usual.

The process as here described has given us the results stated in the table below. No determinations which have been made by this method have been omitted. Steels Nos. 1, 2, and 3 were kindly furnished us by Dr. Dudley, and are the same as those described in this JOURNAL, 16, 217, and the gravimetric determinations given are the very careful ones reported in that paper. Steel "a" was also furnished us by Dr. Dudley with the statement that it contains, by their determination, 0.016 per cent. phosphorus, and is the lowest they have. Steel C is a tool steel containing, probably, about one per cent. of carbon, and, by our own gravimetric determination by the combined acetate-molybdate-magnesia method<sup>1</sup>, using ten grams of the steel, 0.021 per cent. of phosphorus. Steel A is a mild steel containing about 0.17 per cent. carbon and, by the molybdate-magnesia method, using five grams, 0.129 per cent. phosphorus. We do not place as much reliance on this gravimetric determination as on the other.

The gravimetric determinations for the cast iron were made as follows: one gram of the iron was dissolved in fifty cc. of nitric acid (1.18) and treated exactly as in our directions for steel. The ammoniacal solution of the yellow precipitate was made up to 150 cc. and two portions of ten cc. each were taken for reduction. These portions gave determinations 18-21 of the table. The remainder of the ammoniacal solution was concentrated in a platinum dish and then precipitated with magnesia mixture.

<sup>1</sup> This JOURNAL, 16, 221.

The magnesium pyrophosphate, after weighing, was dissolved in hydrochloric acid and evaporated to separate silica. In the first determination no silica was found; in the second there was an appreciable amount. The gravimetric determinations gave 1.75 and 1.79 per cent. of phosphorus, respectively.

In order to determine if more phosphorus could be obtained by solution in aqua regia, one gram of the iron was dissolved in thirty cc. of a mixture of equal volumes of concentrated nitric and hydrochloric acids; the solution was made up to 150 cc.; ten cc. were placed in a porcelain dish with five cc. of concentrated nitric acid, evaporated to dryness, and heated to 200° for one-half hour, the residue taken up with fifty cc. of nitric acid (1.18), nineteen cc. of ammonia added, and the solution precipitated as usual. This method gave the determinations 22 and 23 of the table. Determinations 24 and 25 of the table were made by the method recommended above for cast iron.

	Gravimetric determination.	Volumetric determination.
1. Steel No. 1.....	0.040 per ct.	0.037 per ct.
2. " " 1.....	0.040 "	0.040 "
3. " " 1.....	0.040 "	0.041 "
4. " " 1 <sup>1</sup> .....	0.040 "	0.0404 "
5. " " 2.....	0.053 "	0.0512 "
6. " " 2.....	0.053 "	0.0548 "
7. " " 2.....	0.053 "	0.0526 "
8. " " 3.....	0.032 "	0.0317 "
9. " " 3.....	0.032 "	0.032 "
10. " " "a".....	0.016 "	0.0177 "
11. " " "a".....	0.016 "	0.0174 "
12. " " C.....	0.021 "	0.021 "
13. " " A.....	0.129 "	0.129 "
14. " " A.....	0.129 "	0.129 "
15. " " A.....	0.129 "	0.127 <sup>2</sup> "
16. 2 gram steel No. 1 + 0.0173 gram. 'cryst. sodium phosphate.....	0.115 "	0.116 "
17. 2 gram steel No. 3 + 0.0231 gram cryst. sodium phosphate.....	0.132 "	0.133 "
18. } 1 gram cast iron.....	1.75	} 1.743 "
19. } " " " ".....		} 1.767 "
20. } I " " " ".....	1.79	} 1.761 "
21. } " " " " ".....		} 1.782 "
22. } I " " " dissolved in aqua regia ...		} 1.755 "
23. } " " " " ".....		} 1.743 "
24. } I " " " " as for steel.. ...		} 1.750 "
25. } " " " " ".....		} 1.745 "

<sup>1</sup> Determination by W. A. Noyes.

<sup>2</sup> With fresh, colorless, molybdic solution.

These determinations furnish, we believe, satisfactory proof that the method which has been described, secures a practically complete precipitation of the phosphorus, even when the amount present is only 0.02 per cent., and also that the ratio of phosphorus to molybdenum in the solution is constant and independent of the amount of phosphorus present; also that the ratio is not affected by the presence of silicon or arsenic in the solution. The cast iron used contains 0.84 per cent. of silicon. As regards arsenic, we have applied Marsh's test for arsenic to the yellow precipitate obtained from two grams of steel No. 2, and obtained only a very faint arsenic mirror, much fainter than that obtained under the same conditions, from 0.02 mgm. of arsenious oxide. If we suppose the arsenic to have been present in a compound analogous to the phosphorus compound, the molybdenum associated with it would correspond to only 0.0003 per cent. of phosphorus. The determinations with the cast iron also furnish evidence that the conversion of phosphorus into phosphoric acid is as complete by solution in nitric acid and oxidation with potassium permanganate as by solution in aqua regia and evaporation with nitric acid. The volumetric determinations with the cast iron are more accordant than the gravimetric. In view of the great difficulties known to exist in the way of securing pure magnesium pyrophosphate, we believe the volumetric determination will usually be found to be more accurate.

TERRE HAUTE, December 20, 1894.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.<sup>1</sup>

BY THOMAS H. NORTON.

Received December 24, 1894.

I have felt it desirable on this occasion to direct your attention to a brief review of the services which the chemist has thus far rendered in the battle with fire, to the field of investigation still open, to the methods of testing and experimentation in this branch, and to the application of fact already gained to American conditions. In the choice of this subject, I have, in common

<sup>1</sup> Abridged from the author's opening address before the Section of Chemistry of the American Association for the Advancement of Science, at the Brooklyn Meeting, August, 1894.

with some of my predecessors, left the domain of pure science to consider more closely certain economic aspects of chemistry, and enter, to some extent, into the province of chemical engineering, which is now recognized in our leading schools as entitled to distinct and separate treatment. A further reason which has influenced me is the practical absence, to this time, in our works of reference, of any attempt to collate and classify the knowledge gained in this field.

The total annual loss of insured property by fire is about \$200,000,000, and of this sum nearly one-half occurs in the United States,—\$90,344,075 in 1893. Foreigners marvel at this reckless disregard of the immense losses by fire shown by our countrymen, for from eighty to ninety per cent. of the 15,000 fires which occur annually, can be traced to easily preventable causes, and chiefly to faulty construction. Consider, for a moment, the tax which is being paid this Moloch. Our total loss of property amounts to one-fifth of the net profits of all the industries of the country. Propose to a trader or manufacturer coolly to throw one-fifth of the annual profits into the grate! Yet this is what our productive industries, as a whole, have been and are doing in an unconcerned, if not cheerful, manner. The direct loss by conflagration is, however, not the only factor. Our fire departments and water supply cost us \$30,000,000 annually; while the loss of wages to mechanics and other productive forces, and numerous contingent amounts, swell the actual total loss to a most serious sum. The fire department of London costs but one-third of that of New York City; and the same ratio applies to most European cities. During a residence of ten years in French and German cities, I saw the fire engines called out but five times; while the average resident of an American city is apt to witness a call at least once a week. England's annual fire bill is but little over \$10,000,000.

With these facts in view, is it not time to call a halt, to bring all the forces of science to bear in the battle, and redeem our America from what is nothing more or less than a servile bondage?

If we seek the reason for this vast difference in relative fire loss between the Europe of to-day and America, it is not to

be found in a superiority of facilities for extinguishing conflagrations. The equipment of American fire departments is far better than that of the fire departments abroad. It results simply from the fact that the European architect and builder have profited from the experience of the past, and learned that prevention is better than cure. The prevalent method of construction in New York is such, architects assure me, that the business part of the city awaits only the proper combination of circumstances to be the scene of a conflagration rivalling that of Chicago.

Before leaving these general considerations, it should be said that there are many hopeful indications of an awakening from this apathy, and ample recognition should be made of the earnest effort, inaugurated of late years in New England, to lessen fire risk; the application of the so-called slow-burning principle of construction, especially to factories. By the adoption of this principle it has been possible to reduce insurance rates from one and one-half to two and one-half per cent. down to two-sevenths of one per cent.

#### FIRE EXTINGUISHERS.

Passing to the more specific treatment of the subject, we find that, as in medicine, so in the matter of protection against loss by fire there are two distinct lines of action: prevention and cure, or the adoption of such measures as to render an outbreak of fire difficult, and a conflagration practically impossible; and the provision of the proper facilities for the rapid subjugation and limitation of fire under full headway. As in medicine, also, there is a growing conviction that the prophylactic treatment is the more important. It is hence particularly in this direction that the activity of the chemist has been chiefly called into play.

Let us first briefly review the methods of extinguishing fire.

In this field but little has been done to add to the efficacy of the agent used from time immemorial—ordinary water. In addition to its cheapness and universal distribution, water possesses, over other liquids, peculiar advantages for the purpose in view—high specific heat and the formation of a vapor which is non-poisonous. Sulphur dioxide has been used to some extent; in fact it is an old-fashioned method in European countries to

extinguish burning chimneys by kindling sulphur on the hearth. A quicker production of the gas is effected, more particularly for use in confined spaces, by introducing receptacles of burning carbon disulphide; and cylinders of liquid sulphur dioxide, have, under similar circumstances, been successfully employed. The advantage in the use of this gas consists entirely in its exclusion of the air necessary to maintain combustion. The slower diffusion consequent upon high density renders it superior for this purpose to other available gases. This advantage is, however, largely counterbalanced by its irritant, poisonous nature, and it has never been accepted as one of the recognized agencies of general application.

Of much greater value is carbon dioxide, the efficacy of which is likewise based upon its ability to prevent the access of air to the material in process of combustion. The ease with which this is accomplished is shown by the familiar experiments of our lecture courses in chemistry. For practical results in dealing with ordinary fires, it is found best to employ a highly charged aqueous solution of the gas. Such solutions as those prepared for use as a beverage, have frequently been used in emergencies. One large soda-water establishment has been able to extinguish several fires in its own factory and in the neighborhood by the prompt use of the carbonated water in its receptacles. A quick-witted pharmacist recently extinguished a serious fire in his store from benzene, by quickly using a pailful of soda-water drawn from his own fountain, the case being one in which simple water would have failed to accomplish the purpose.

The so-called chemical fire-engines, now regularly used in our public fire departments, are all constructed upon the principle of charging a quantity of water when used with carbon dioxide and ejecting a stream of the carbonated water by the pressure of the gas itself. In the size most frequently employed the supporting truck carries two cylindrical tanks of steel or copper, holding about eighty gallons of water and twenty-eight pounds of sodium bicarbonate with a leaden jar containing fourteen pounds of sulphuric acid. At the moment of using, by a simple mechanical device, the acid is admitted to the solution and a pressure of 140 pounds to the square inch is developed. The



tanks are charged alternately while in operation so that it is possible to maintain a continuous jet of one-fourth of an inch. The whole apparatus is light and easily drawn by two horses. There is also in use a combined manual and chemical fire engine devised by Foster. The pumps fill, with water, the compartments in which the chemicals are dissolved and whence the solutions come together in a generating chamber where the gas is evolved. Such engines are capable of throwing per minute thirty gallons of water containing 250 gallons of carbon dioxide to a distance of ninety feet. This type is also arranged for connection with high pressure mains. Very careful tests carried out in 1883 showed conclusively the great value of a small quantity of carbonated water in extinguishing fierce flame, especially in a confined situation and when combustion had not penetrated much beneath the surface. The same principle was applied earlier by Baragwanath and others in a variety of forms, to portable extinguishers. Dick's extinguisher, largely used in England, is a cylindrical tank of seven gallons, easily carried on the back, giving a pressure of from 70 to 120 pounds, and possessing a projectile range of fifty feet. The peculiar feature of this type is the storing of the sulphuric acid in a glass container, which is easily broken when the apparatus is to be used. Zabel's apparatus, like Dick's, is charged with sodium bicarbonate, but the acid used is contained in a cylinder from which it is liberated by simple inversion. Devices, essentially the same, have been introduced by Masnata and VanWisker. In Carter's extinguisher the sulphuric acid is replaced by tartaric acid.

Platt's extinguisher has been successfully used for many years, and is valued on account of its simplicity; the turning of a valve and the inversion of the apparatus bringing it at once into operation. Other efficient extinguishers of American origin are the Babcock, the Harkness, and the "Climax." In the latter, sulphuric acid is replaced by oxalic acid, and in both the Harkness and "Climax" the carbonated solution is forced out by a pump. The Babcock extinguisher is filled with a solution of sodium bicarbonate, and has in its upper part a vessel of acid suspended by lateral pivots to a stirrup depending from the top of the apparatus. The stopper of this vessel is worked by a rod

through the top of the extinguisher. By withdrawing the stopper, the vessel tilts over and mingles the acid with the solution producing at once the necessary pressure.<sup>1</sup>

The most recent and perhaps most efficient of chemical extinguishers is that introduced in 1893 by Dr. Henry P. Weidig, and extensively tested throughout our country during the past twelve months. It is adapted not only for portable use, but also for replacing ordinary town engines and for permanent installation in factories and on board ships, etc.

The apparatus consists of a steel vessel containing liquid carbon dioxide so arranged that it may be brought in connection with a receptacle filled with carbonated water, or a solution of ammonium carbonate, under any desired pressure. The carbonated water meets in its exit pipe with a stream of ammonia gas emanating from a cylinder of liquid anhydrous ammonia. The carbon dioxide is thus bound in the form of a soluble salt, ammonium carbonate. The solution thus formed is forcibly ejected, and, on reaching a fire, the heat not only volatilizes the water but decomposes the salt, so that a mixture of steam, carbon dioxide, and ammonia is the result. One volume of water will yield under these circumstances twenty-five volumes of the two latter gases.

The principle of rapidly filling a confined space where fire has broken out with inert gases has been extended to the use of the gaseous products issuing from the combustion under boilers. In certain industrial establishments devices are introduced by which the current of the mixture of nitrogen, carbon dioxide, and aqueous vapor can be directed, at will, into a given apartment. The results are quite effective, combustion being promptly and permanently stopped. Other additions than carbon dioxide to the water used in extinguishing fires have proved of doubtful utility when submitted to practical tests. The list of such proposed additions includes potash (Kaiser), clay (Glaser), a mixture of sodium sulphite, and four parts sodium alum (patented 1884 in Austria, by Trotha, and sold in the form of cartridges), salt, alum, waterglass, copperas, Glauber's salt, borax, magnesium chloride, sodium phosphate, and soda.

<sup>1</sup> Hexamer, *Journal of the Franklin Institute*, August, 1885.

Ammonia gas alone has been recommended. Its lightness and irritant properties render it, however, much less efficient than carbon dioxide or sulphur dioxide.

Hand grenades,<sup>1</sup> consisting of glass bottles, usually of a spherical form, charged with aqueous solutions of various chemicals, have found their way of late years into somewhat extended use. They are conveniently arranged in the corridors of large buildings, and are intended for use in extinguishing incipient outbreaks of fire. The grenade is to be thrown with such force into the center of combustion that it breaks and scatters its contents upon the burning material. The salts present are supposed to act by either giving off incombustible gases or by incrusting the burning articles, thereby excluding air. In practice, however, it is found that these grenades render but slight service, as they are frequently unbroken when thrown, especially *against* non-resistant substances. They are supposed to be charged with strongly carbonated water, or with a saturated solution of ammonium chloride, sodium chloride, sulphite, or thiosulphate. Analysis, however, shows quite a variety of composition in the contents. Sir Frederick Abel,<sup>2</sup> in 1881, found one to contain a strong solution of salt and waterglass. Geissler examined three current types with the following results:<sup>3</sup>

*Hayward's Grenade.*—Gross weight 1,120 grams; weight of liquid, 750 grams; composition, an aqueous solution of 15.7 per cent. calcium chloride and 5.6 per cent. magnesium chloride.

*Harden's Grenade.*—Gross weight, 900 grams; weight of liquid, 555 grams; composition, an aqueous solution of 19.5 per cent. sodium chloride, and 8.9 per cent. ammonium chloride.

*Schonberg's Grenade.*—Gross weight, 770 grams; weight of liquid, 440 grams; composition, an aqueous solution of 1.66 per cent. sodium carbonate, and 6.4 per cent. sodium chloride.

It may be noted in passing that the salts in these grenades cost about one per cent. of their selling price.

Finally, mention should be made of extinguishing powders,<sup>4</sup> the use of which is literally a fighting of fire with fire. They

<sup>1</sup> Hexamer, *loc. cit.*

<sup>2</sup> Amer. Arch, 13 and 14.

<sup>3</sup> Pharm. Centrbl., 1885, 447.

<sup>4</sup> Hexamer, *loc. cit.*

are well devised to produce, by rapid combustion at the expense of the oxygen in saltpeter, a sufficient volume of inert gas—chiefly sulphur dioxide and carbon dioxide—to prevent the circulation of air about a fire, and thereby cut off the supply of atmospheric oxygen for further combustion. Their application is, of necessity, limited to small enclosed spaces without many openings for ventilation, and they have been found chiefly valuable in drying rooms where easily volatile products are being driven off, as in connection with the manufacture of oilcloth. The ingredients are coarsely powdered and readily ignited. They are often packed in cartridges and provided with fuses. They burn without explosion, with a bright white flame, a strong odor, and much smoke. Each pound yields about four and eight-tenths cubic feet of gas, which consists of two and three-tenths sulphur dioxide, one and one-tenth parts carbon dioxide, and one and four-tenths parts nitrogen. One pound should be used for every 240 cubic feet of an enclosed space. The composition of the best known of these powders is as follows:

<i>Bucher's powder</i>	{	KNO <sub>3</sub>	60 parts.
		S	36 "
		C	4 "
<i>Heeren's powder</i>	{	KNO <sub>3</sub>	63 parts.
		S	29 "
		C	4 "
		Fe <sub>2</sub> O <sub>3</sub>	4 "
<i>Schweizer's powder</i>	{	KNO <sub>3</sub>	58 parts.
		S	36 "
		C	3 "
		Fe <sub>2</sub> O <sub>3</sub>	1½ "
		SiO <sub>2</sub> (sand)	75 "
<i>Gruneberg's powder</i>	{	KCl	20 parts.
		KNO <sub>3</sub>	50 "
		S	50 "
		MnO <sub>2</sub>	1 "
		Rosin	10 "
<i>Zeisler's powder</i>	{	KNO <sub>3</sub>	60 parts.
		S	36 "
		C and CaO	4 "

<i>Johnston's powder</i>	{	Equal parts of KCl, KNO <sub>3</sub> , MnO <sub>2</sub> and Rosin, moistened with waterglass and pressed into briquettes.
<i>Phillips' Fire Annihilator</i> (introduced in 1851.)	{	KNO <sub>3</sub> 60 parts. C                        20 " CaSO <sub>4</sub> + 2H <sub>2</sub> O    5 "

This latter was pressed in the form of a hollow brick. The central cavity contained sugar, and potassium chlorate and a vial of sulphuric acid, the latter so arranged as to be easily broken by a simple mechanical device. The brick was usually placed within a double cylindrical receiver containing water, so that the ignition of the powder caused not only the evolution of a large volume of gas, but also, by its heat, a liberation of a considerable amount of aqueous vapor.

In reviewing this portion of our subject it would appear that but few opportunities are afforded the chemist for further contributions of value. It would seem advisable, however, to study the feasibility of extending the use of carbon dioxide along lines similar to those in which automatic sprinklers have found such satisfactory application. In many factories and in numerous stores and warehouses the sprinkler, while most effective in quenching flame or hampering its progress, causes serious damage to manufactured products or materials for manufacture. The advantages of carbon dioxide over water under these conditions are manifest. It is not difficult to conceive of a system of piping, opening naturally at the level of the floor, through which either automatically or under the control of a watchman, a powerful current of the gas could be directed into any apartment where flame was apparent. In the many cases where the losses by water do and would naturally far exceed the losses by direct combustion, there is but little doubt that the use of the invisible, inert, harmless gas would enormously limit the destruction of valuable property.

We come now to the most important division of our subject; namely, the methods of preventing loss or suffering by fire through the use of structural materials, textile fabrics, and the like, which are either entirely incombustible or slowly combusti-

ble or from which the property of rapid combustion has been largely removed by special treatment. A structure built entirely of stone, brick, iron, cement, etc., is an illustration of the first type. A structure of brick with heavy beams of wood, heavy floors of plank, no hidden air-spaces, and a general absence of the lighter forms of woodwork, illustrates the second type,—the slow combustion construction. The third type is to be found in an edifice of wood, the component parts of which, either by impregnation or by suitable coatings, have lost the property of ready inflammability.

The study of the choice of materials and their most efficient grouping as employed in the first and second methods of construction, apart from architectural considerations, falls purely within the domain of the mechanical engineer. It involves the question of strains and stresses under ordinary conditions and under the conditions of an elevated temperature.

It is in the special field of rendering such easily combustible substances as wood and the vegetable fibers used in textile fabrics more or less resistant to flame that the chemist has been able to render service.

Could our methods of building be limited to the completely fire-proof or the slow-burning system of construction, and interior decoration and equipment be restricted to the use of non-combustible materials, it is evident that the chemist would have but little to do. But mechanical considerations, canons of taste and questions of outlay will, for a long time to come, sustain the extended use of wood in the erection and finishing of many classes of edifices, especially of our homes. The beginnings of our towns and cities are almost entirely in wood, and the same may be said of the suburbs of our centers of population. It will be many years before the rural residence and the home of the laborer in America will be as universally constructed of non-combustible materials as in Great Britain, France, Germany, and other European countries. In such a country as Japan it is almost impossible to imagine any general departure from the time-honored and picturesque national construction of bamboo. The restriction of fabrics to fibers of animal origin is likewise out of the question.

In noting the historical development of the work of the chemist in the field as above outlined, we will first consider the methods which have been applied to textile fabrics and paper, and next those which have been used to render wood unflammable.

#### TREATMENT OF TEXTILES AND PAPER.

The first experiments in this direction were made in England in 1735 by Obadiah Wild,<sup>1</sup> who secured a patent for rendering the cartridge cases used by the navy resistant to flame. This process consisted of the addition of a mixture of alum, borax, and copperas, to the paper pulp employed. Early in the present century the subject attracted the attention of several chemists. De Hemptine, of Belgium, in 1821, made quite an extended study of mixtures, similar to that of Wild, and other substances. At the same time Brugnatelli recommended the use of potassium silicate, Hermbstadt of ferrous sulphate, De Lisle of an unnamed compound.<sup>1</sup> Gay Lussac<sup>2</sup> was deeply interested in the subject. In 1830, as the results of his experiments, he recommended the use of various chlorides, phosphates, borates, tartrates, and carbonates without, however, considering the difficulties involved in their application on a large scale. The employment of the alkaline carbonates was later urged strongly by Prater, while Fuchs<sup>1</sup> and Bethel in 1838 advocated waterglass and others, gypsum. Several patents were taken out during this period by the different investigators. Still later Chevalier recommended the use of a mixture of borax and ammonium sulphate. The use of ammonium sulphate alone was proposed by De Breza in 1838, and that of ammonium chloride by Froggatt in 1857. In 1855 M. Solomon,<sup>3</sup> of Paris, submitted to the English Board of Ordnance a process for rendering canvas unflammable. It consisted of immersing the materials for a day in each of the following baths:

I. Aluminum sulphate, 30 parts. II. Dry calcium chloride, 20 parts

Glue (gelatin),	10	“	Glue,	10	“
Water,	60	“	Water,	70	“

<sup>1</sup> Versmann and Oppenheim, Report to the British Association, 1859

<sup>2</sup> *Ann. chim. phys.*, 18, 211.

<sup>3</sup> *Amer. Arch.*, 13 and 14.

[TO BE CONTINUED.]

## THE ACTION OF ORGANIC AND MINERAL ACIDS UPON SOILS.

BY HARRY SNYDER.

Received January 2, 1895.

IN soil analysis, the hydrochloric acid use for dissolving the potash, lime, and phosphates has a specific gravity of 1.115. This acid is used because it is supposed to represent, practically, the same solvent power which agricultural plants possess in obtaining their food from the soil. Inasmuch as this premises is the foundation of a part of the present system of soil analysis, it is a question of the greatest importance. One of the indications which points to the truth of the premises is the similarity of the action of hydrochloric acid of this strength, and of organic acids upon samples of soil.

*Organic Acids.*—In some of the soil work which has been in progress in the chemical laboratory of the Minnesota Experiment Station, the solvent action of the various organic acids has been determined with another ultimate object in view. Incidentally, the results give sufficient data for the comparative action of the organic acids and of hydrochloric acid, sp. gr., 1.115, upon the same samples of soil.

Different types of soil are acted upon quite differently by the various organic acids, and general conclusions regarding their action upon various types of soil can not be stated. Hence the statements which are made upon this question have reference only to the type of soil under consideration.

The figures given in the table were obtained from a soil sample taken from one of the rotation plots at the Experiment Station. In obtaining the solutions for analysis, oxalic, tartaric, and citric acids, of ten per cent. strength, by weight, were used. The digestion was carried on for thirty-six hours in the Snyder soil flask as used at this station. The organic acid mixture was made by preparing a ten per cent. solution, by weight of citric, oxalic, and tartaric acids. The material soluble in the organic acids was separated by filtration and washing. The solution was then gently ignited to remove the organic acids, so that the analysis could be completed in the usual way.



Ten per cent. solutions were used because the more concentrated ones crystallized upon standing, and, then too, preliminary trials indicated that the more concentrated organic acid solutions possessed less solvent power than those here used. One difficulty experienced in the work was obtaining tartaric acid free from potash, and citric and oxalic acids free from lime. All of the determinations were made in duplicate, and controlled by blank determinations.

TABLE I.

SOLVENT ACTION OF HYDROCHLORIC AND ORGANIC ACIDS UPON A SOIL.

	Hydrochloric acid 1.115 sp. gr.	Ten per cent. solution of			
		citric acid.	oxalic acid.	tartaric acid.	organic acid mixture.
Total insoluble, per cent....	84.08	87.90	85.07	87.67	85.93
Potash.....	0.30	0.12	0.18	0.06	0.10
Soda.....	0.25	0.17	0.19	0.05	0.12
Lime.....	0.51	0.50	0.23	0.41	0.45
Magnesia .....	0.26	0.27	0.21	0.32	0.33
Iron oxide .....	2.56	1.59	1.14	1.62	2.23
Alumina .....	4.24	1.45	3.96	1.77	2.99
Phosphoric anhydride.....	0.23	0.26	0.14	0.11	0.26
Sulphuric " .....	0.08	0.10	0.05	0.06	0.05

The oxalic acid caused an increase in the solubility of the alumina. There is a marked difference between the solvent action of these three acids. The oxalic acid possesses the greatest solvent action upon the complex insoluble matter of an alkaline nature. The citric acid possesses the greatest solvent action upon the lime, magnesia, and the sulphuric and phosphoric anhydrides. The amount of lime dissolved by the oxalic acid is greater than would, at first, be expected, but the complex nature of the solution, and the presence of the salts of other metals, has caused nearly half as much lime to be dissolved by the oxalic acid as by the hydrochloric acid of sp. gr. 1.115.

The ten per cent. mixture of the three organic acids has resulted in dissolving as much phosphates and magnesia, and nearly as much lime as any one of the acids acting alone. The potash does not appear to be as soluble in the organic acid mixture as the other elements of plant food.

The amount of potassium, iron, and aluminum oxides, dissolved by these three organic acids and their mixtures is somewhat less than that dissolved by the hydrochloric acid. The

iron and alumina are not of any economic importance in interpreting the results of soil analysis. The main difference between the solvent action of the hydrochloric and the organic acids is in the somewhat smaller amount of potash dissolved by the organic acids.

With the exception of the solubility of the potash, as noted, these results bring out, in a general manner, the value of hydrochloric acid of 1.115 sp. gr. as a solvent, over the organic acids, of ten per cent. strength, because the hydrochloric acid represents the limit of the solvent action reached by any one of the organic acids acting alone or in a mixture.

For the purpose of comparison, the solvent action of hydrochloric acid, sp. gr. 1.115, and the maximum limit reached in any case, by the organic acids, are given, together with the name of the acid possessing the highest solvent power for that constituent.

TABLE II.

	Hydrochloric acid, sp. gr. 1.115.	Largest amount dissolved by organic acids.	Name of the organic acid.
Total insoluble, per cent.....	84.08	85.07	Oxalic
Potash.....	0.30	0.18	Oxalic
Soda.....	0.25	0.19	Oxalic
Lime.....	0.51	0.50	Citric
Magnesia.....	0.26	0.27	Citric
Iron oxide.....	2.56	2.23	Mixture
Alumina.....	4.24	3.96	Oxalic
Phosphoric anhydride.....	0.23	0.26	{ Citric and Mixture
Sulphuric ".....	0.08	0.10	

*Mineral Acids.*—The action of the concentrated mineral acids upon the same sample of soil is given in Table III. Concentrated hydrochloric acid, forty per cent. strength, dissolved two and a quarter per cent. more of the complex silicates than nitric acid of the same strength. Concentrated nitric acid possesses a stronger solvent action than the dilute hydrochloric acid. The concentrated hydrochloric acid dissolved somewhat more potash than the hydrochloric acid of 1.115 sp. gr. The amount of lime, phosphates, and sulphates, dissolved by the concentrated hydrochloric acid, was about the same as when the more dilute acid was used; the concentrated acid, however, dissolved more of the complex silicates of potash, iron, and alumina. Sulphuric acid possesses the strongest solvent action.

Of the total potash in the soil, as determined by fusion, less than eighteen per cent. is soluble in the hydrochloric acid as used in soil analysis; about ten per cent. is soluble in oxalic acid, and three per cent. in tartaric acid.

TABLE III.

	CONCENTRATED ACIDS.			
	Hydrochloric acid.	Nitric acid.	Sulphuric acid.	Total by fusion methods.
Total insoluble, per cent.....	81.20	83.45	80.45	72.45
Potash.....	0.42	0.30	0.52	1.75
Soda.....	0.31	0.28	0.40	0.50
Lime.....	0.55	0.30	0.53	0.86
Magnesia.....	0.40	0.32	0.52	0.72
Iron oxide.....	3.41	2.97	3.57	3.63
Alumina.....	5.84	4.55	6.88	12.71
Phosphoric anhydride.....	0.23	0.23	0.26	0.28
Sulphuric ".....	0.08	0.08	0.10	0.10

## NEW BOOKS.

A TREATISE ON INDUSTRIAL PHOTOMETRY, WITH SPECIAL APPLICATION TO ELECTRIC LIGHTING. BY A. PALAZ, PROFESSOR OF INDUSTRIAL ELECTRICITY IN THE SCIENCE FACULTY OF THE UNIVERSITY OF LAUSANNE. TRANSLATION BY GEO. W. PATTERSON, JR., ASSISTANT PROFESSOR OF PHYSICS IN THE UNIVERSITY OF MICHIGAN, AND M. R. PATTERSON. pp. 322. New York: D. Van Nostrand Co., 1894. Price, \$4.00.

Many of the methods of photometry which have been long in use for measuring the intensity of light from gas flames have required modification when applied to the measurement of the intense light produced by electricity. A book which gathers together and arranges, systematically, the work on the subject which is scattered in many different journals, and which is frequently difficult of access, will be very welcome to many who are interested in the subject.

The first part of the book gives a discussion of the general principles of photometry and includes a description of all of the common photometers and photometric standards. This part of the book is quite full and will be of value to anyone interested in photometry in any of its applications. Then, follow chapters on the equipment of photometric laboratories, and on the measurement of the intensity and distribution of light from electrical sources.

In an appendix of eight pages the translators criticise or give additional information upon a few topics in the book.

The work of translation appears to have been carefully done, and the English used by the translators is good. A short index is given, which might be made more comprehensive with great advantage. There are a great many short references to particular topics, and to the work of individuals, which can not be found by means of the index.

W. A. NOYES.

**DESCRIPTIVE INORGANIC GENERAL CHEMISTRY. A TEXT-BOOK FOR COLLEGES.** BY PAUL C. FREER, M.D., PH. D. (MUNICH), PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN. Revised edition. pp. 550. 54 Illustrations. Boston: Allyn and Bacon. 1894. Introductory price \$3.00.

This book is intended as a text-book for colleges and is therefore adapted for the use of students who already have some knowledge of the elementary principles of the science. The treatment of the subject is consequently somewhat different from that usually pursued in the best of the recent text-books on chemistry. For example the book begins with a discussion of the atomic theory and the composition of chemical compounds. The author believes that "beginners should be taken through a course in which only a few elements and compounds are discussed, with the purpose of familiarizing the pupils with the fundamental laws which govern chemical change." "During the progress of such work as this," he continues, "I would not advise the use of chemical symbols or any reference to the atomic theory. It is manifestly impossible to make a student without experimental knowledge, understand, in all its bearings, a theory which it has taken some ninety years to place upon its present footing. If an elementary course, in which every stated fact has been proved by actual experiment, precedes the work given in this book, the pupil will be then amply fitted to look at chemical phenomena from the basis of the atomic theory."

Professor Freer is undoubtedly right in this matter and the sooner the teachers of chemistry in this country recognize the truth contained in the above-quoted statements and model their instruction on the plan there suggested the better it will be for the teaching of the science of chemistry in our colleges and uni-

versities. If the teaching of the elements of the subject could be relegated to the secondary schools, where it properly belongs, then it would be possible to give a very much more satisfactory course in chemistry in our colleges and universities on the lines laid down by Dr. Freer in the present book.

In the descriptive part of the work the author has used the last editions of Graham-Otto's "*Lehrbuch der Allgemeinen Chemie*," and Ladenburg's "*Hardwörterbuch der Chemie*," though the original articles in the chemical journals have been freely consulted. The elements have been discussed, in general, in the order in which they occur in the periodical system and the attempt has been made to show the influence exerted by the nature of the elements which form a chemical compound.

The book must be regarded from all points of view as a very good one and one that can be highly recommended for use in our colleges and universities. The facts are stated clearly, concisely, and correctly, and the latest information obtainable on the subject is always presented. Teachers of chemistry will find the book full of new ideas and suggestive of the relations of the various phenomena to one another that are usually overlooked in the ordinary text-book on the subject.

What the author has to say on the subject of valence in the preface to the book is very interesting. He says: "My views upon the subject of valence and the use of structural formulas may probably be regarded as too conservative by many of my colleagues, but I have been led to adopt these views by the growing conviction that the dogmatic use of supposed laws of valence and of constitutional formulas founded upon very incomplete experimental evidence, is causing more harm than good to the advancement of chemical science." Most of the teachers of chemistry will endorse the latter part of this statement. The author has made free use of the facts derived from the domain of the so-called physical chemistry wherever he has thought it advisable, and he has thus been able to present reasons for our views of certain chemical phenomena which would be otherwise perfectly inexplicable to the student.

Notwithstanding the general excellence of the book it has some minor faults. The use of the word not-metal throughout

the work when the word non-metal is in general use by chemists seems ill-advised and unwarranted. The same statement may be made also with reference to the word not-conductor. Hydroiodic acid and stibional are used instead of the more usual hydriodic acid and antimonyl and for no apparent reason. Hydrazine, hydroxylamine, azoimide, and methine are written without the final *e* probably because that is the German way of spelling these words and the author is more familiar with them in German than in English. No reference whatever is made to the preparation of the diamond artificially by Moissan and, in speaking of the preparation of the acid  $\text{HN}_3$ , the simplest and best method of all that have been proposed, *viz.*, that of Wislizenus, by the action of nitrous oxide on sodium amide, is entirely omitted.

On page 278, near the bottom, occurs the following remarkable statement: "By a judicious combination of the iodides of organic radicles, carbon and hydrogen compounds containing as many as sixty *carbonates* in a molecule have been prepared." In a foot-note, Hill and Hägele are made responsible for this "judicious combination," but it is doubtful if these chemists would recognize their own statement in this form.

$\text{HN}_3$  is referred to as azoimide or hydrogen nitride and the salts of the acid are called nitrides. It would seem to the reviewer that a name which recalled the fact that the substance was an acid, would be preferable, and, since there are quite a large number of nitrides known which are certainly not salts of the acid  $\text{HN}_3$ , much unnecessary confusion will be introduced by the use of the word nitride for a salt of the acid  $\text{HN}_3$ . These are, however, but slight faults which may be readily corrected in the next edition of the book and that another edition of so excellent a work will soon be called for seems highly desirable and also highly probable.

The book is singularly free from typographical errors, is well printed and well bound, contains a useful appendix of laboratory notes intended as a guide to teachers and students in compiling a list of experiments, and last, but by no means least, a very complete index.

W. R. ORNDORFF.

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### THE SYNTHETIC FOOD OF THE FUTURE.<sup>1</sup>

BY HARVEY W. WILEY.

THE problem of human nutrition is the great groundwork of sociology. I use the word nutrition in its broadest sense, including clothing and fuel, which, while not as essential as food to life, are quite as important factors in civilization. Until within a few years the study of nutrition and the means of providing it have been deemed the exclusive function of agriculture. In the development of this idea, we have seen springing into existence in all parts of the civilized world, within the past twenty-five years, colleges of agriculture and agronomic experiment stations in large numbers. Especially in this country have we seen the greatest activity in this line. In all the states and territories, fostered by the federal government, schools have been established in which instruction in agriculture has been made a fundamental branch of the college curriculum. There are fifty-seven agricultural experiment stations in the United States. Each state and territory has at least one. Louisiana has three, Alabama, Connecticut, Massachusetts, New Jersey, and New York each two, and the Department of Agriculture two, one in Florida and one in California. For the support of the state and territorial stations, Congress has made an appropriation for the fiscal year ending June 30th, 1895, of \$745,000 and for the Department stations \$10,000, in all \$755,000. The agricultural colleges in the states and territories have also been endowed by

<sup>1</sup>Retiring Address of Harvey W. Wiley as President of the Society, Boylston Hall, Harvard University, Dec. 28, 1894.

grants of public land proportionate in extent to the numbers of senators and representatives in congress. The annual money value of these grants varies with their extent and the wisdom with which they have been invested, but the total sum is approximately a million and a half dollars. In addition to this a sum of money is granted annually to each agricultural college directly from the treasury, and this sum is to be increased at the rate of \$1000 per annum until it amounts for each institution to \$25,000 a year. This amount will be reached in five years. At present the total sum so granted is nearly a million dollars, and it will soon be a million and a quarter. The total amount of the financial aid thus granted directly from the treasury to the agricultural colleges and experiment stations is at the present time approximately three million and a quarter dollars annually. To this must be added the amount given directly by the states and arising from private endowments—a sum of no inconsiderable importance. In all it may be said that about four million dollars in this country are annually devoted to the promotion of agricultural and allied education and research, a sum more liberal than that devoted by any other country to similar objects.

The natural result from such investigations is an increase in soil productiveness, the reclamation of lands supposed heretofore to be unfit for tillage and a greater economy of food production. The supply of human food, therefore, appears to more than keep step with the increase in population and food consumption. In so far as economic reasons extend, there is no occasion to look outside of scientific agriculture for the supply of human food.

But another view is presented of the subject of a more strictly scientific aspect, based on the remarkable progress which has been made in the past few years in the domain of synthetic chemistry. The year 1828 marks a new era in the history of chemistry. It was in this year that Wöhler succeeded in making synthetic urea by the union of cyanic acid and ammonia. Urea is not of a high order of organic bodies; in fact, it is a result of retrograde action in the living organism and the consequent result of the breaking down of higher organic bodies; yet its artificial formation was a brilliant victory of chemical methods, a bold and successful charge



on the breastworks of organic compounds. To change the figure, it was the crossing of the dead line which had been drawn previously between the living cell and the inanimate crucible. The line once having been crossed, the old distinctions between the organic and the inorganic world have been completely obliterated. With them have gone also the divisions which were supposed to separate the animal from the plant. It is now known that animals do not get their entire nourishment from so-called organic nor plants from inorganic compounds. Many plants, especially those free of chlorophyl, live alone on organic compounds. Especially noteworthy among these, from the character of the chemical activity which they manifest, are the vegetations of a bacterial nature, living largely on organic products. Even the green plants first fabricate the inorganic elements into organic compounds before taking them into their tissues. The green cells are the tiny kitchens in which the meals of the plant molecules are prepared.

Without dwelling on further details of this subject, it is sufficient for the present purpose to state that the progress of modern science has entirely changed our ideas respecting the sharp lines of division which were formerly thought to exist between the animal and vegetable, and between the nature of artificial chemical compounds and those produced by biochemical action in the living organism. We stand, therefore, face to face with the fact that it is possible to produce, by artificial means in the laboratory, compounds which have heretofore been the results of exclusive biochemical functional activity of living organisms.

One remarkable fact in connection with Wöhler's synthesis of an organic compound is of interest here. While all the chemical world wondered at Wöhler's achievement, nearly fifty years elapsed before this rich field of chemical progress was further cultivated to any extent, with the single exception of the synthesis of acetic acid by Kolbe, in 1845. But since that time remarkable progress has been made. It is not my purpose here to recite in detail the synthetic accomplishments of Berthelot, Kekulé, Kolbe, Maumené, Baeyer, Hoffmann, Frankland, Ladenberg, Fischer, and many other celebrated workers in this field.<sup>1</sup>

<sup>1</sup> See Rise and Development of Organic Chemistry, by C. Schorlemmer, revised edition, 1894.

For the purpose of the present paper, only two points in organic chemical synthesis need be considered; *viz.*, first, the economy of the process, and second, the probability of the production of food compounds suited to the nourishment of man.

In respect of the first point, we find many illustrative examples of synthetic products which are furnished at so small an expense as to practically exclude from the market the corresponding natural articles. Among these may be mentioned salicylic acid made artificially by Kolbe's process. Salicylic acid occurs as a natural product in the flowers of *Spirea ulmaria* and as a methyl ether in the oil of wintergreen (*Gaultheria procumbens*). It can be formed by synthesis in various ways, as, for instance, by fusion of salicylaldehyde with potassium hydroxide. Salicine, coumarine, indigo, cresol, or toluenesulphonic acid may be substituted for the salicylaldehyde. When phenyl carbonate is heated with a caustic alkali, salicylic acid is also produced. It may also be obtained when an alkaline solution of phenol is boiled with carbon tetrachloride. But none of these processes, although of great interest chemically, have any value commercially save that of Kolbe, or more properly, Kolbe and Lautemann, which consists of passing carbon dioxide into sodium phenylate.

But it will be observed that the phenol which is the base of the process, is itself an organic compound, or the result of the destructive distillation of an organic compound produced by nature. It is not impossible to produce phenol by artificial synthesis. It is said that by surrounding the points of an electric arc light with hydrogen that carbon and hydrogen combine to form acetylene,  $C_2H_2$ . According to Berthelot,<sup>1</sup> fuming sulfuric acid absorbs acetylene and the product so formed fused with caustic soda forms phenol or sodium phenate. But it needs no further illustration to show that a phenol formed in this manner could never, on account of its great cost, be used for the commercial manufacture of salicylic acid.

A distinction should be made in this matter between the formation of possible food products by synthesis from existing organic natural bodies, and the synthesis which begins with the inorganic elements themselves. The transformation of one organic

<sup>1</sup> *J. prakt. Chem.*, 2, 10, 93.

<sup>2</sup> *Compt. rend.*, 68, 539.

body into another of greater value to human industry is quite a different matter from the building up of organic bodies without the help of a living organism. Berthelot himself, who is now the apostle of synthetic foods, summarizes the steps which will probably be traversed on the way which is to end in the substitution of the chemist for the farmer:

1. Hydrocarbons, obtained by the union of hydrogen and carbon.
2. Alcohols formed from the hydrocarbons in various ways.
3. Aldehydes and acids obtained from alcohol by oxidation.
4. Amides produced by the action of ammonia on the alcohols.
5. Alkaloids formed by the action of ammonia on the alcohols and aldehydes.

But even granting the fullest development of such a scheme, the impartial observer will be compelled to admit that there is still an immense gulf between the best of the products formed and human food.

In the case of medicines and drugs, perhaps the case is more hopeful. In so far as mere transformation of one organic substance into another of greater therapeutic value is concerned, much progress has already been made. But in nearly all of these cases the products are obtained by the splitting up of more complex into less complex molecules. In other words, it is a retrograde synthesis and not a constructive one. A mere list of remedies in common use, which have been formed in this way, would form an extensive index of pharmacy.

Both Liebig and Wöhler, as early as 1837, foresaw this advance in synthetic chemistry and predicted the synthesis of alkaloids and antiseptics and even of sugar.

Founded on the classical researches of Williamson on etherification has been built the art of forming by synthesis a great variety of flavoring matters for food and drink. In the strict sense of the term, these condiments are not foods inasmuch as they are not subject to digestion and do not take any part in the nourishment of the tissues. They have a nearer relationship, however, to the purpose of this address than the bodies already mentioned.

The slow natural oxidation of the alcohols in fermented and dis-

tilled drinks, giving rise to ethers of delicate odor and flavor, is an expensive process, and synthetic chemistry has boldly come to the aid of nature. The essences of fruits and flowers are now elaborated in great numbers in our laboratories and supply to a certain extent the natural products. With the aid of ethyl alcohol, burnt sugar, and a collection of artificial essences, the skillful manipulator will mix, in short order, drinks which resemble bourbon and old rye, madeira and sherry. The pure fruit flavors of many soda-water fountains could easily prove an alibi in respect of orchards. In the great majority of cases these essences are also the products of retrograde synthesis, or have for the base of manufacture an alcohol derived from the fermentation of a natural sugar. While it is true that they can be manufactured at a lower cost than attends their natural production, and while they are used as condiments in foods and drinks, yet in no sense can they be regarded as a step toward the preparation of foods from inorganic elements by purely chemical means. The principal artificial flavoring extracts are the derivatives of the fatty acids, especially the ethers and aldehydes. The ethereal salts of acetic, valerianic, benzoic, salicylic, and butyric acids, are the most common of these bodies. Methyl, ethyl, and amyl are the bases most usually found in the above compounds. Vanillin has also been made synthetically. Analysis showed that this natural product of the vanilla fruit was methylprotocatechuic aldehyde. This knowledge led to its artificial production. From turpentine is derived a perfume turpineol which is known as "lily of the valley." The artificial production of musk and of the perfume of the violet have also been accomplished.

Whether or not these bodies are injurious to health is a question whose discussion can not be entered into here. In the case of one of the best known of these condiments, and one which is not of ethereal origin, it may be said that its use in foods is prohibited in some countries, whether it be used as a sweetener or as an antiseptic. In justice to saccharin, however, it should be stated that repressive legislation against it has been quite as much due to a feeling of jealousy on the part of beet-sugar producers as to a suspicion of unwholesomeness on the part of the medical fraternity. Certain it is, however, that, even as a sweet-

ener, it will never take the place of sugar and because of its antiseptic properties it must necessarily interfere to some degree with the action of the digestive ferments.

It is not necessary to take up in detail other synthetic compounds which have attained a commercial success. The artificial dye stuffs are types of these bodies and illustrate, in a most brilliant manner, the progress of chemical synthesis based on the knowledge of the internal constitution of organic compounds derived from analytical investigations. But even the most enthusiastic believer in the future triumphs of chemical science will fail to find anything more than an inspiration in these achievements in respect of the production of foods. In all cases of coloring matters, original organic compounds derived from living cells, or the products of their destruction, have served as the bases of the processes. Without an elaborate review of this field therefore, and which, moreover, has already been made,<sup>1</sup> we pass at once to consider these achievements in synthesis which relate directly to the matter under consideration.

Along two lines of especial interest to food production, synthetic chemistry has made its greatest advances; *viz.*, the production of glycerides and of sugars. Wurtz<sup>2</sup> has described a method of synthesizing glycerol, which, in logic, would be called arguing in a circle.

Tribromhydrine,

HCHBr

CHBr, is decomposed with silver  
HCHBr

acetate forming triacetine. This is saponified by baryta yielding glycerol. The tribromhydrine, however, is first prepared from glycerol or rather from allyl iodide made from glycerol. At the end of this long synthesis, therefore, the chemist is exactly on the spot whence he started. Friedel and Silva<sup>3</sup>, however, made glycerol in a different way. Trichlorhydrine is prepared from propylene chloride and saponified by heating with water. The propylene used is made from acetone. Wagner<sup>4</sup> produced glycerol by oxidizing allyl alcohol with potassium permanganate.

<sup>1</sup> *Ber d. chem. Ges.*, 1891, 24, 1007.

<sup>2</sup> *Ann. Chem.* (Liebig), 102, 339.

<sup>3</sup> *Bull. Soc. Chim.*, 20, 98.

<sup>4</sup> *Ber d. chem. Ges.*, 21, 3351.

Glycerol has also been formed synthetically by other investigators, but the principles involved are not greatly different from those set forth.

The first notice I have seen of the artificial formation of a fat is in a paper by Pelouze and Gelis<sup>1</sup> published in 1844. It is said that by gently heating a mixture of glycerol, butyric acid, and strong sulphuric acid, and afterwards diluting with water a yellowish oil separates. This fat is not soluble, or only slightly so, in water. It is soluble in all proportions in strong alcohol and in ether. Caustic potash breaks it up into butyric acid and glycerol. It may be formed at ordinary temperatures by passing a current of hydrochloric acid into a mixture of butyric acid and glycerol and afterwards diluting. The authors thought this body to be the butyrine discovered in butter by Chevreul. Its great solubility in alcohol would lead us in this day to suppose that the body was not a true butyrine.

Our present knowledge of the natural fats is based almost solely on the classic researches of Chevreul. While the work of Chevreul was purely analytic in its character, the knowledge of the constitution of fats which it disseminated has been the foundation on which all subsequent structures have been built. While at the present day chemists do not recognize the existence of margaric acid and margarine, all the other fatty bodies described by Chevreul have been found to have substantially the constitution which he assigned them.

Berthelot's first important contribution to the synthesis of fats was presented to the French Academy of Sciences on the 5th of September, 1853. It was entitled "Memoire sur les combinaisons de la glycerine avec les acides et sur la synthese des principes immediats des graisses des animaux."<sup>2</sup> From Berthelot's paper we learn that glycerol was discovered in 1779 by Scheele<sup>3</sup> in making lead plaster.

Fourcroy was the first to theorize on the nature of fats<sup>4</sup>.

Berthelot regarded the formation of soap as due to the affinity of oils for alkali.<sup>5</sup>

<sup>1</sup> *Ann. chim. phys.*, 1844, [3], 10, 434.

<sup>2</sup> *Ann. chim. phys.*, 1854, [3], 41, 216.

<sup>3</sup> *Opuscula*, 2, 175.

<sup>4</sup> *Système des connaissances chimiques*, 7, 142, 323, 329, and 334.

<sup>5</sup> Chevreul, *Ann. chim. phys.*, 88, 226.

Fourcroy in his work on the fat of cadavers, substituted another idea for this rational one, thinking the formation of soap due to the oxidation of the oil under the influence of alkali and air. He classed the vegetable oils, waxes, cadaveric fats, fats liberated from soaps by acid, cholesterine, etc., together under the name "adipocere."<sup>1</sup>

In 1815, simultaneously with the discoveries of Chevreul, Braconnot rejected the ideas of Fourcroy, saying :

"When tallow is agitated with acid or alkali, the three constituents, hydrogen, oxygen, and carbon, which had been in a state of equilibrium, separate and rearrange themselves in another order, giving rise to adipocere and to a very fusible fat, soluble in alcohol."<sup>2</sup>

Pelouze produced sulphoglyceric acids and phosphoglyceric acids and together with Gelis<sup>3</sup> he made butyrine, the first artificially prepared fat.

Berthelot has generalized this work by combining glycerol with both organic and inorganic acids. The bodies produced are, as a rule, neutral and incapable of directly uniting with alkali. Some reproduce the natural fats.

*Stearins*.—Stearic acid, melting at  $70^{\circ}$  and prepared according to the method of Chevreul,<sup>4</sup> forms with glycerol three neutral bodies, mono-, di-, and tristearin. The last is identical with natural stearin. To make monostearin; Berthelot heats equal parts of glycerol and stearic acid to  $200^{\circ}$  for thirty-six hours in a sealed tube. The body formed is insoluble in glycerol and readily separates from the excess of this body. It may be purified by heating to  $100^{\circ}$  with ether and quicklime to deprive it of excess of stearic acid.

To make distearin: This body may be formed by heating equal parts of glycerol and stearic acid to  $100^{\circ}$  for 114 hours, or to  $275^{\circ}$  for seven hours. It may also be formed by heating natural stearin to  $200^{\circ}$  for twenty-hours in the presence of glycerol. Another method is to heat monostearin to  $260^{\circ}$  for three

<sup>1</sup> *Ann. chim. phys.*, 3, 129; *Ibid.*, 5, 154; *Ibid.*, 8, 17, 23, 31, and 67.

<sup>2</sup> *Ann. chim. phys.*, 93, 271.

<sup>3</sup> Sur la acide sulfoglycerique, *Compt. rend.*, 21, 718; Sur la butyrine, *Nouvelles, Ann chim phys.*, 10, 455.

<sup>4</sup> *Recherches sur les corps gras*, page 206.

hours in the presence of three parts of stearic acid. However formed, it is to be purified by the treatment with ether and lime.

To make tristearin: This body is obtained by heating monostearin to  $270^{\circ}$  for three hours with fifteen or twenty times its weight of stearic acid. Water is eliminated. The product is to be purified with ether and lime. The properties of natural and artificial stearin coincide as nearly as can be expected, considering the fact that natural stearin is never obtained pure. The nearest approach in properties by natural stearin to those of the artificial, was that shown by a preparation made by P. Duffy<sup>1</sup> who purified it by thirty-two crystallizations. The acid prepared by saponification, etc., from the synthetic stearin had the same melting-point as that originally employed.

*Margarines.*—Margaric acid from human fat<sup>2</sup> forms two neutral combinations with glycerol, monomargarine, and trimargarine.

To make monomargarine: Monomargarine may be prepared by heating a mixture of glycerol and margaric acid to  $200^{\circ}$  for twenty-one hours or to  $100^{\circ}$  for 106 hours. The reaction takes place with great readiness, in fact the synthesis is easier than that of any other fat. The same body or a similar one, is formed by simple contact of the constituents at ordinary temperatures for three months, though in very small quantity. A margarine is also formed by heating a mixture of margaric acid and glycerol saturated with hydrochloric acid, to  $100^{\circ}$  for some hours, but it is always contaminated with chlorhydrine.

Trimargarine is formed by heating monomargarine to  $270^{\circ}$  for seven hours in the presence of excess of margaric acid. The fat acid separated from it by saponification, etc., had the same melting-point as that originally employed.

*Palmitins.*—Three palmitins were formed in the way employed for the preceding fats.

*Oleins.*—Three were formed. The oleic acid employed was purified by the method suggested by Gottlieb.<sup>3</sup> The commercial acid was twice chilled and filtered and then converted into a potash soap. The soap was dissolved in twice its weight of alco-

<sup>1</sup> *Quart. Jour. Chem. Soc.*, Jan., 1853, pages 303, 309, 310.

<sup>2</sup> Chevreul, *Recherches, sur les corps gras*, page 59.

<sup>3</sup> *Ann. der Chem. u. Pharm.*, 57, 93.



hol, filtered cold, and precipitated with barium chloride. The barium soap was recrystallized from boiling alcohol (one liter of strong alcohol dissolves five grams), and then decomposed by tartaric acid in an atmosphere of hydrogen.

Valerines, butyrines and acetines were formed in the same general manner.

All these fats could also be produced, and more easily, by heating the components to  $100^{\circ}$  in the presence of an auxiliary acid, such as sulphuric, hydrochloric, tartaric, phosphoric, etc. Triacetine has also been formed by Böttenger<sup>1</sup> by the action of acetic anhydride on glycerol in the presence of acid potassium sulphate.

In this direction the work of molecule building has been carried a step further in securing the construction of a higher glyceride containing phosphorus. Hundeshagen<sup>2</sup> has succeeded in preparing a substance similar to lecithin, which is one of the essential constituents of cell plasma. In this work he followed first in the steps of Berthelot in securing distearin (distearyl glycerol) by heating stearic acid with an equal volume of anhydrous glycerol for thirty hours in closed tubes at  $200^{\circ}$ . The purified distearin, heated to  $110^{\circ}$  with metaphosphoric acid or phosphoric anhydride, gave the desired phosphorus compound. Numbers of the salts and derivatives of the distearyl glycerol phosphoric acid have also been prepared and studied.

In the matter of sugars greater progress has been made. The elder Thenard, more than fifty years ago, proposed a scheme for the direct production of sucrose by the condensation of carbon dioxide, water, and ethylene. Kiliani, Tollens, and many others have made important contributions to this work, but by far the most important advances in the synthesis of sugars have been made by Fischer. His work has been most thoroughly reviewed in this country by Keiser<sup>3</sup> and Stone.<sup>4</sup> Fischer<sup>5</sup> has also published a résumé of his work. Starting with formaldehyde and passing through glycerol and acrolein, Fischer, by a series of beautifully conceived researches, has succeeded in forming,

<sup>1</sup> *Ann. Chem.*, 263, 359.

<sup>2</sup> *J. prakt. Chem.*, neue Folge, 28, 219.

<sup>3</sup> *Am. Chem. J.*, 11, 277, and 12, 357.

<sup>4</sup> *Ag. Science*, 6, 166.

<sup>5</sup> *Ber d. chem. Ges.*, 23, 2114, and 27, 3189.

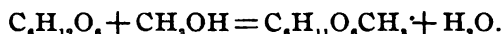
by synthesis, a large number of sugars, some of which have not been discovered in nature. For the details of this work, the reviews mentioned can be consulted.

Lately in the same direction, another step has been taken. Fischer and Bunsch<sup>1</sup> have shown that the sugars under the influence of hydrochloric acid in the presence of alcohols and oxyacids are condensed to polysaccharides resembling glucosides.<sup>2</sup> Of these bodies methyl glucoside,  $C_6H_{11}O_5CH_3$ , methyl arabinoside,  $C_5H_9O_4CH_3$ , ethylarabinoside,  $C_5H_9O_4C_2H_5$ , ethylglucoside,  $C_6H_{11}O_5C_2H_5$ , methylgalactoside,  $C_6H_{11}O_5CH_3$ , ethylgalactoside,  $C_6H_{11}O_5C_2H_5$  and benzylarabinoside,  $C_5H_9O_4CH_2C_6H_5$ , have already been formed.

Previous to the appearance of the above papers, Michael<sup>3</sup> had described a method for the synthesis of a glucoside. This method depends on the interaction taking place between so-called acetochlorhydrose and the alkaline carbolates. The method yields only a moderate product and is somewhat troublesome.

The process employed by Fischer in converting sugars into glucosidal bodies is well illustrated by the following example:

Grape sugar is dissolved in methyl alcohol and in the cold the solution is saturated with gaseous hydrochloric acid. The solution soon loses its power to reduce alkaline copper under this treatment and a crystalline product is formed. The reaction which takes place is represented by the following formula:



To this substance the name methyl glucoside is given. The other bodies named above are formed by similar reactions.

Fischer, however, freely admits that although synthesis has done so much in the way of producing compounds which heretofore have been deemed the exclusive product of living vegetable cells, yet in the case of sugars an essential difference still exists.<sup>4</sup> In the laboratory there is produced at first only an inactive sugar which afterwards, by means of special operations, is split up into the active modifications, while the assimilation

<sup>1</sup> *Ber d. chem. Ges.*, 27, 2478.

<sup>2</sup> *Ber d. chem. Ges.*, 26, 2400.

<sup>3</sup> *Compt. rend.*, 89, 355.

<sup>4</sup> Oration before the Institute for Military Surgeons, August 2, 1894, *Neue Zeitschrift für Rübenzucker-Industrie*, 23, 185.

process of plants gives directly the active sugars of the same geometrical series. The stereochemistry of the carbohydrates, however, furnishes for this fact a full explanation.

If, in the case of an active sugar, by means of hydrocyanic acid, an additional carbon atom is added, the artificial process takes place in an asymmetric way. Since now in plant assimilation the optically active constituents of the chlorophyll granule take part in the production of carbohydrates, it is easy to understand how from the beginning, the formation of sugars with six carbon atoms takes place in an asymmetric manner.

In so far as I have been able to determine, no experiments have been made to determine the digestive coefficient of these synthetic foods. In the case of the artificial sugars many of them are unaffected by alcoholic ferments and it is safe to assume that the digestive ferments would be equally powerless to disintegrate them. The direct products of sugar synthesis are, as a rule, neutral to polarized light. This does not imply that morphologically they are so different from the natural products, but rather that the carbon asymmetry is inversely twinned and the product is composed of equal quantities of right and left-handed sugars.

Of the natural sugars, levulose is the only left-handed one of any economic or digestive importance. The specific rotatory power of this body varies with the temperature, and at 88° the disjointed carbon atoms are so much reduced in position as to show a rotatory power equal to that of dextrose.

So far, it does not appear that the left-handed sugars made by synthesis have all the properties of levulose. They seem to be somewhat different in their stereometric relations from the natural product. In fact, the theory does not require that the left-handed sugars be levulose, but that they be simply the twin asymmetric duplicates of the right-handed varieties. Left-handed dextrose, therefore, is an entirely different substance from levulose. For the old name dextrose, Fischer uses glucose, and for levulose, fructose. The prefixes l., d., and i., signify left and right polarizing and inactive respectively. In one case, however, he has discovered a. d. fructose as well as a. l. glucose.

We have seen how by slow and painful steps and by round-

about ways the synthesis of sugar has gradually progressed until products containing nine molecules of carbon have been obtained. The ordinary sugar of commerce, saccharose, contains a molecule with twelve atoms of carbon. This sugar, however, can not be strictly considered as a dodekose, for it appears to be the product of the condensation of two hexoses. Whatever may be the true theory of its composition, whether wholly of the aldehyde type or a hybrid aldehyde ketone, yet its structure is of a higher order than the simple hexoses and it has not been formed artificially by any of the usual processes of synthesis.

It has remained for an inventor to take a short cut across the synthetic field and make saccharose *per saltum*.

Jean Ercole Pelligrini, a citizen of Italy, residing in France, has taken out a patent in this country for making sugar in a thoroughly direct manner. Ethylene gas, carbon dioxide, and steam are admitted in proper proportions to a channeled cube of pumice stone, impregnated with platinum sponge. The carbon dioxide and ethylene are used in practically equal volumes and the steam *ad libitum*. The pressure is so regulated that each gas will gradually diffuse through the whole porous platinized space. The operation is continued for about half an hour and "at the end of this period" to quote the language of the letters patent, "a sirup containing from twenty to twenty-five per cent. of sugar is withdrawn."

A sample of the sirup submitted with the application for the patent was examined in the laboratory of the Division of Chemistry at Washington and found to be sucrose. That it was made in the manner described, however, is a matter which, to my mind, requires further demonstration. The examiners of the Patent Office were, nevertheless, assured of the genuineness of the sample, by what proof I know not. For my part, I do not believe that a single molecule of sucrose can be made by that process. Some simple organic acid might be produced in this way, possibly some inactive sugar, but where shall we look for the stereochemical asymmetry which is so predominant a feature in that complex molecule which we call saccharose?

But for the sake of argument, grant the actual production of this substance. The price of a pound of carbon dioxide is far

greater than that of a pound of sugar, and ethylene is still far more expensive. If the process of Pelligrini really works as well as the United States has certified, the sugar would cost nearly a dollar a pound. The whole process, in my opinion, may be classed with the electrical refining methods so successfully employed a few years ago in scientific buncoing. A full exposition of the fallacies of the method is given by Maumené.<sup>1</sup>

In the foregoing pages I have attempted to give a synopsis of some of the forms of organic synthesis which would enable us to come to a definite opinion regarding the possible production of artificial food. The prospect, it must be admitted, is not a flattering one.

First of all, it is seen that all cases of successful synthesis from an economic sense, belong either to the class already mentioned, *viz.*, retrograde synthesis, or to a process depending on the use of already existing organic compounds.

In this direction chemistry has a wealth of future achievements to offer commerce. The changes and modifications which can be made in natural products will continue hereafter, as in the past, to present to chemical science problems of the most promising success. As in the case of the polysaccharide starch, from which a simple hexose sugar is produced of the widest use in the arts, so with other organic products of the field, many victories in retrograde synthesis may be won. Chemistry will show how to make many foods more useful, and in the way of cooking more nutritious and palatable. In respect of the direct or indirect union of the elements into successful food products, there is not a single instance in all that have been cited to give any hope whatever.

In the way of economy the simple synthesis of hydrogen and nitrogen to form ammonia has never seen any chance of economic success. Here in one way, at least, synthesis might help to increase the stores of food. Nitrogen in ammonia salts is now worth eighteen cents a pound to the farmer. A simple synthesis would materially reduce its price. It might be well for the ambitious chemist to begin with ammonia before attempting albumen. While the scientific difficulties are less formidable

<sup>1</sup> *Jour. de Fab. de Sucre*, 35, No. 4.

than the economic ones, yet they are apparently unsurmountable. A single pound of synthetic sugar must be worth many dollars, and we do not know that it will submit itself to digestion. The complex molecules of albuminoids and starches seem to me to be beyond the reach of chemical handicraft. There is no possibility of making many of the nutritive constituents of porter-house steak, much less the mixing of them into an attractive and tempting form. In the field of scientific research, however, and the light which will be thrown on molecular structure, there are no limits to the triumphs of synthetic chemistry.

As the periodic law among the elements, so the theories of stereostructure, isomerism, asymmetry, and condensation have led and will lead to the greatest discoveries. When the investigator is once convinced of the possibility of any compound he will never cease to look for it until its discovery crowns his efforts. As the disturbance caused by an unknown body in space leads the astronomer to train his glass on the unexplored depths of the heavens, so do the missing links in molecular structures incite the chemist to renewed exertions. This fact is beautifully illustrated in the case of the carbohydrates. In the last few years there have been added to the number of sugars known to be produced by nature, more than twenty built by synthesis. But large numbers of possible sugars are still missing.

According to Fischer,<sup>1</sup> every asymmetric carbon atom in a carbohydrate molecule makes two forms possible. There can, therefore, be at least eight hexoses, and each of these is optically paired, making sixteen in all. Ten years ago only two of like structure of this number were known. Now ten have been discovered, and six yet remain unknown. Of the pentoses there are eight possible forms, of which four have been discovered. Of the thirty-two possible heptoses, only six are known, and of the 128 nonoses, only two. Since the possible number of compounds increases in a geometrical ratio with the addition of carbon atoms, it is seen that the field for discovery is not soon likely to be exhausted. But the molecule builder, it seems certain, must take his stones from Nature's quarries. He may fashion and change them, adapt them to new uses and endow them with more

<sup>1</sup> Neue Zeitschrift für Rübenzucker-Industrie, 23, 169.

valuable properties, but he can not make them of the raw original materials.

Schorlemmer in the revised edition of his *Development of Organic Chemistry*, while taking a very sanguine view of the future progress of synthetic chemistry, does not expect it to interfere with the farmer. He expects, at most, morphia and quinia to come from the laboratory instead of from the poppy and cinchona.

Roscoe says: "But now the question may be put, is any limit set to this synthetic power of the chemist? Although the danger of dogmatism, as to the progress of science, has already been shown in too many instances, yet one can not help feeling that the barrier which exists between the organized and unorganized world is one which the chemist at present sees no chance of breaking down.

It is true that there are those who profess to foresee the day when the chemist by a succession of constructive efforts, may pass beyond albumen and gather the elements of lifeless matter into a living structure. Whatever may be said regarding this from other standpoints the chemist can only say that at present no such problem lies within his province. Protoplasm with which the simplest manifestations of life are associated is not a compound but a structure built up of compounds. The chemist may successfully synthesize any of its component molecules, but he has no more reason to expect the synthetic production of the structure than to imagine that the synthesis of gallic acid leads to the artificial production of nutgalls."<sup>1</sup>

It seems strange, therefore, that one of the most eminent of living chemists should have so unequivocally committed himself to the doctrine of future synthetic foods.

In an address before the Society of Chemical and Mechanical Industries in Paris, on the 5th of April, 1894, Berthelot publicly proclaimed his theory of the coming suppression of agriculture and the substitution of synthetic foods for its products. This theory he has more fully elaborated in McClure's Magazine for September 1894. The accomplishments in synthetic chemistry on which he bases his predictions are essentially those which

<sup>1</sup> Presidential Address, British Association, *Chem. News*, Sept. 2, 1887, p. 100.

have been set forth already in this address. With proverbial European provincialism, however, he fails to mention one of the strongest of the arguments he might have used; *viz.*, Fischer's sugar synthesis. The wildcat process lately patented in this country, however, as well as in France, for making sugar by the condensation of ethylene receives favorable mention and no doubt is entertained of the speedy manufacture of sugar on the largest scale synthetically and that the culture of the sugar-beet and sugar-cane will be abandoned because they will have ceased to pay. The struggling sugar planters of our own country who during the present season have been making sugar at a cost of four cents a pound and selling it for three, will bear witness to the fact that this happy period has already arrived.

The synthesis of the dyestuffs, especially of alizarin and indigo, he cites as examples of the destruction of an agricultural industry by chemical achievements. He dwells, and very properly, on his own work in the synthesis of fats as evidence of what may be accomplished in that line. The beefsteak of the future may not be identical with that of to-day, but it will be a tablet of any color or shape desired and will entirely satisfy the epicurean senses of the year 2000. Chemistry has developed the whole science of cookery and flavoring and provided all the utensils of the kitchen. It remains now only for it to complete its work and furnish the food itself. Even at the present time, according to Berthelot, tea and coffee could be made artificially if the necessity should arise. The caffeine of the chemist has the following genealogy:

Carbon and oxygen beget carbon dioxide.

Carbon dioxide and chlorine beget carbonyl chloride.

Carbonyl chloride and ammonia beget urea.

From urea comes uric acid.

From uric acid is derived xanthin.

Xanthin yields theobromine.

Theobromine yields theine or caffeine.

From this pedigree it is concluded that tea plants, and cocoa and coffee trees will soon follow the madder and indigo plants into economic eclipse. No attempt is made to compute the cost of the caffeine necessary for a single cup of Java; and the fact that caffeine is only one of its constituents is naively ignored.



Tobacco also is soon to follow because something resembling nicotine has already been made synthetically. While nicotine has not yet been made synthetically, its near relationship to conine, the active principle of hemlock, which has been so formed, leaves little doubt of the speedy accomplishment of this desirable end.

In regard to the synthesis of food products directly from the elements attention is called to the following points :

By means of the electric spark acting on hydrogen and carbon at a white heat, acetylene is produced.

Acetylene will combine with another atom of nascent hydrogen forming ethylene and marsh-gas.

Ethylene can be made to combine with the elements of water forming common alcohol, while marsh-gas in similar circumstances, yields methyl alcohol.

Acetylene with nascent oxygen forms oxalic acid.

Acetylene in contact with nitrogen subjected to the electric spark forms hydrocyanic acid.

Acetylene and oxygen in the presence of water and an alkali form an acetate, whence acetic acid.

"I also found," says Berthelot, "that ethylene under certain conditions could be transformed directly into benzene. Here then we have seven familiar compounds of wide utility; acetylene, marsh-gas, alcohol, oxalic acid, acetic acid, cyanhydric acid, and benzene, to say nothing of many others which I might mention obtained from these elements direct. Now imagine for a moment the enormous number of organic compounds into the constitution of which, according to regularly acting laws, these seven different compounds enter. There are six different families of alcohols alone and each one of these families embraces a greater or less number of special alcohols. Over the whole field of organic chemistry the mystery of possibilities extends. Its combinations and intercombinations are so limitless that we can only work on regularly to ends that it is impossible to foresee."

According to Berthelot, the fields which are now defaced by agriculture will be beautified by regaining their natural covering and the earth will be one vast park of pleasure and the chemist the great conservator of the human race.

A synthetic climate will replace the capricious one furnished by nature. Winds and waterfalls will provide power and light, and the bowels of the earth, tapped by frequent wells to a great depth, will supply the superheated steam to turn the winter into spring and to bring together the pole and the equator. When these predictions are read we first think that Bellamy has turned chemist, and by reincarnation in the shape of the great Parisian Savant has thrust upon the scientific world a new edition of "Looking Backwards."

In all the instances brought forth there is not the slightest approach to anything to justify the prophecy of a period of artificial food. The few cases of synthesis in which the products approach the composition of anything digestible present such insurmountable difficulties in expense and supervision as to render any expectation of reaching economic results utterly futile. In the great majority of cases, as has been seen, the process of synthesis is conducted on materials already organized by living cells. The enormous cost of building up any kind of a commercial, synthetic organic body directly from the elements is such as to render it, in my opinion, utterly improbable of successful achievement.

Even if food products can be formed in the crucible there is no reason whatever for supposing that they can ever play any rôle in an economic sense. The untold billions of laboratories which nature builds are infinitely cheaper in construction and operation than those filled with platinum and porcelain. The sun ignites the crucibles of nature at an expense far less than attends the use of the city gas works. The director of Nature's laboratory depends on no endowment nor legislation for his salary and his bills for supplies are not disallowed by any board of auditors on the score of economy. Night and day his patient faithful assistants work without thirst for fame, without hope of reward. They fight not for priority of discovery and their anonymous papers are printed in rich profusion in the great *Berichte* of the universe. The chemistry of the chlorophyll cell is far more wonderful than any of the achievements of Lavoisier, Berzelius, or Fischer.

It would doubtless be a solace to the weary toiler in the sun to

look forward to a time when he might lie in the shade while proteids were pricking up their ears in the condenser and fats frying in the scientific pan. But in the days of the far future, while Berthelot will still be honored and Fischer praised, the farmer will be found following in the furrow, fields of waving grain will brighten the landscape, and herds of kine graze upon the hills.

*Members of the Society :*

According to the provisions of our Constitution, the time has arrived when I am to take my leave of you as President of the Society. I thank you most heartily for the honor twice conferred upon me of presiding over this great organization. It is only fitting at this moment that I should give a brief account of my stewardship.

One of the most gratifying features in connection with the history of the Society during the past two years, is the increase in membership. In two years, according to the data furnished by the Secretary, the Society has more than doubled its membership. Our membership now is well up to the thousand mark. I should have been better pleased at this time to take leave of a membership of fully 1,000, but I feel sure that this number will soon be reached.

The JOURNAL of the Society has fully kept pace with the increase of membership. The volume for 1893 contains 720 pages, devoted almost exclusively to original articles, of which 98 appeared. The volume for 1894 contains 891 pages, exclusive of proceedings, and 158 original articles. In addition to the copies furnished the members of the Society, there is a large number of subscribers to the journal in this and foreign countries, so that the total circulation at the present time is over 1,000. It is recognized as a leading chemical journal by the editors of foreign periodicals. More than thirty of its articles, during the past year, have been reprinted wholly or in part in the *Chemical News*, and a large number of abstracts has appeared in the *Journal of the English Society*, the *Berichte*, and the *Central-Blatt*, in which, during the past twelve months, over 100 abstracts of articles from the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY have appeared. These are figures which are very gratifying to us all.

The prosperity of the Society has been due to united action among all its members, and a determination to make it a success.

Local Sections have been established during the past two years in Washington, the Lehigh Valley, and in New Orleans. The chemists of the Pacific Slope have also expressed a desire to unite with the Society at an early date and establish a Local Section. There are many other places where the membership of the Society would justify the establishment of Local Sections, and especially is this true of Baltimore, Philadelphia, Boston, Cleveland, and Chicago, and it is hoped that speedy action may be taken to secure these desirable results.

To the editor and the Committee on Publications the Society is indebted for energetic and systematic work in increasing the efficiency of the JOURNAL, but the efforts which these gentlemen have made would have had but little success had not the members of the Society throughout all parts of the country come forward with contributions of papers. There are often good reasons why a paper on any particular subject should be published in a particular journal in this or other countries, but as a rule it seems to me that American authors should first offer their papers to American journals, and if this rule is followed it is certain that the journal of our own Society will receive a fair share of the contributions. We would not desire to exclude from the field any other journal, but we are justified in asking that due consideration be given our own journal by our members in the distribution of their papers.

The American Chemical Society represents American chemical science as a whole and therefore it is desirable that the journal of the Society should not become the organ of any particular branch of chemical science. The editor and the Committee on Publications have kept this end in view in the distribution of the articles and have endeavored to put into each number something of interest to many of the special departments of chemical science. Our doors are open for the entrance of those engaged in didactic chemistry, for organic chemists, for technical chemists, for agricultural chemists, for mining and assaying chemists, for general manufacturing chemists, and in fact for every branch of our great science. The journal being thus cosmopolitan brings to every

chemist not only matter relating particularly to his branch of study, but also a general idea of what is going on in other fields of activity. He, therefore, who desires to keep abreast of the work of the times and avoid becoming narrow in his views and practices, can not find a better means to this end than membership in our Society. The American Chemical Society has no quarrel with any chemical sect or any institution of learning, but will endeavor to make itself useful to all. It would especially seek to foster a spirit of scientific patriotism in this country, a belief in American science and American scientists, and to diminish, to a certain extent, the blind worship of foreign institutions which, in some instances, has been so characteristic a feature of American workers. I would not say anything to discourage a young man from seeking a part of his education abroad, but I would certainly encourage foreign chemists to seek a part of their education in this country. It is not quite right for the United States to contribute so many students and so few professors. While the American student may find benefit from a course of study abroad, the foreign student would find equal benefit by a residence at some of the great institutions of learning in this country. If professors of chemistry desire to attract students from abroad they must recognize their own country in its scientific institutions. They can not afford to remain outside of the great organized body of American chemists and to send their contributions all to foreign journals if they wish their own institutions to grow in favor at home and abroad. While we are proud therefore, of our large membership, it is evident that for every one who is now a member there are at least two who should become so.

There are nearly 4000 men in the United States who are engaged directly in chemical pursuits, and it is not too much to ask that at least fifty per cent. of this number should become affiliated with the American Chemical Society. We will not consider that we have attained our normal growth if at the end of the next quinquennial period our membership shall not reach fully 2000. To this end let each of our members pledge his word and exert his influence and the work will be accomplished.

I can not close this address without expressing my thanks to

the Secretary of the Society for the efficient method in which he has conducted the work of his office, arduous and exacting as it has been, and to the Directors and Councilors of the Society for the support which they have given me in all matters connected with the executive conduct of the presidential office.

In the little which I myself have been able to do, I have had in view only one object; *viz.*, the welfare and prosperity of the Society. It may be that in some cases offence has been given to members of the Society by the manner in which my work has been done, but I am sure that those who have intimate knowledge of the motives which have actuated my conduct will bear witness to the fact that such offence was not given with malice or meaning.

To my successor I may say that he will find the officers, councilors, and directors, remaining as they do mostly unchanged, full of zeal in the work of building up the Society and ready at all times to support him in the conduct of his office.

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## THE DETERMINATION OF PHOSPHORIC ACID.

BY H. PEMBERTON, JR.

Received January 17, 1895.

THE method of determining phosphoric acid by the alkalimetric titration of the yellow precipitate, has been employed, lately, by a number of chemists and has been made a subject of investigation by the Association of Official Agricultural Chemists. A report upon the subject has been embodied in its last bulletin.

There are a few points regarding this method to which attention should be drawn.

In preparing the standard alkali its strength is, of course, established by testing it against acid of known strength. In doing this, it is important that the indicator used should be phenolphthalein, and *not* methylorange. Potassium hydroxide almost invariably contains alumina, and such a solution gives the neutral reaction with methyl orange *before* it gives it with phenolphthalein. Consequently if methyl orange is used in the standardizing and phenolphthalein is used in the titration of the

yellow precipitate, too much of the alkali will be used in the latter case, and the results will be high.

The same reasoning holds true in case a little carbon dioxide is present in the alkali.

In regard to the precipitation of the phosphoric acid by the aqueous solution of the molybdate, the following directions were given: Heat is now applied, and the solution brought to a full boil. It is then removed from the lamp, *no more heat being applied*. (This JOURNAL, 15, 387.)

I have italicized here in order to draw attention to this point. If the volume of the phosphate solution is from fifty to seventy-five cc., it will be found, after adding five cc. of the molybdate, say three times (fifteen cc. in all) that the temperature of the solution will be about 70° C., which is about the proper temperature for the precipitation. In other words, the solution, once heated, will take care of itself, (if I may use the expression) and does not require a water-bath of definite temperature, or any testings with the thermometer.

There is another point in connection with this precipitation that is of interest. It is well known that a precipitate that has a crystalline or coarse structure is more easily washed, and is less liable to carry down impurities, than a precipitate obtained in a finely divided condition, or as a "mud." Thus in separating lime as sulphate, from iron and alumina, in Jones' process, the alcohol is not added until most of the calcium sulphate has crystallized out from the aqueous solution. Were the sulphuric acid added to the alcoholic solution the precipitate would certainly be impure. In like manner, in potassium determinations, we evaporate the solution nearly to dryness (although it takes this extra time), in order to obtain the platinum salt in a crystalline state. Again in precipitating phosphoric acid by magnesia mixture, the latter is added slowly, drop by drop, "stirring vigorously," in order to prevent contamination. In the same way, when precipitating by the aqueous molybdate, I am accustomed to run the contents of the five cc. pipette into the solution *not* in one continuous stream, but by interrupting the flow from the pipette by momentarily touching the end of the pipette with the finger, *stirring* the solution as it goes in. Thus

the precipitate does not come down *en bloc*, in presence of a great excess of molybdate, but forms in a solution that is comparatively bare of molybdenum until the precipitate is nearly all down. The washing of the precipitate is best conducted, with the use of a vacuum, on a Hirsch porcelain funnel, smallest size, or as described by Mr. B. W. Kilgore, on a porcelain disk, (the disk to be covered with filter paper) with rubber rim in three inch glass funnel. In either case, soft paper from cut filters is better than that bought in sheets. Others have used the Gooch crucible, with advantage. With the Hirsch funnel I find that a precipitate containing forty mgms. of phosphorus pentoxide is thoroughly washed by 300 cc. of water. I may say here that fifty mgms. of phosphorus pentoxide is about the largest quantity that it is well to work upon, when employing a suction-pump. Chemists who do not use suction had better employ not more than thirty to forty mgms. The phosphomolybdate is a difficult precipitate to wash, being like lead chromate in this respect.

The nitric acid, sp. gr. one and four-tenths, and the ammonium nitrate solution, are best kept in graduated glass cylinders of 200 to 300 cc. capacity, the mouths of which are kept covered by small beakers. The quantity desired to be poured out can then be read off on the graduation.

The molybdate solution (which should be neutral, and is best freed from any insoluble molybdic acid by filtration), can be kept in an ordinary narrow-mouth bottle. A wide, flat cork covers the mouth of this bottle, and through the center of this cork the stem of a five cc. volume pipette is held tight. This pipette rests, when not in use, in the molybdenum solution, and the cork prevents the entrance of dust. Mr. Kilgore has applied the ordinary nitric acid solution of the molybdate, to this volumetric process, with good results. He heats the solution on a water-bath having a constant temperature of 60° C. Mr. F. Bergami adds to his solution of the phosphate (containing already about three cc. of strong nitric acid), ten cc. of ammonia, sp. gr. 0.90, and then fifteen cc. of nitric acid, sp. gr. 1.40, and then, after heating to boiling, proceeds with the aqueous molybdate, in the usual way. Mr. L. A. Voorhees, precipitates with the nitric acid solution of the molyb-



date *in the cold*, allows to stand, at the temperature of the room, over night, and titrates in the morning. The details of these modifications are given in the 1894 report of the Association of Official Agricultural Chemists, published at Washington, D. C. Whatever modification may be used, the volumetric method will be found much quicker than the gravimetric, and, after a little experience, fully as reliable.

PHILADELPHIA, Pa.

### ON THE ESTIMATION OF SULPHUR IN PYRITES.<sup>1</sup>

BY G. LUNGE.

Received December 20, 1894.

UNDER the above title, Mr. T. S. Gladding (This JOURNAL, June, 1894); has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole gram of pyrites, I only half a gram; and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (three volumes of nitric acid of sp. gr. 1.42 and one volume of fuming hydrochloric acid) Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for seventy-five grams of potassium bromide can not possibly be dissolved in fifty grams of cold water, or anything like that quantity, but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 cc. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

<sup>1</sup>Read at the Boston Meeting, December 28, 1894.

A more important modification is the following: It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates can not be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Ztschr. anal. Chem.*, 19, 419) I found on the average 0.19 per cent. too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-makers' Handbook," *viz.*, precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride; evidently with the tacit assumption that the small quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-makers' Handbook," and although he entirely adopts the prescription given there (page 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words: "Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have

proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour, that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 cc., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, *viz.*, adding fifty cc. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results: 50.17; 50.42; 50.20; 50.23; 50.19; average, 50.24 per cent. The insoluble amounted to 1.42 per cent; the moisture to 0.47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling), another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:

Gladding's Method.	Lunge's Method.
50.24	50.24
50.24	50.22
50.30	50.28
<hr/>	<hr/>
50.26	50.25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, *viz.*, 50.24. The conclusions to be drawn therefrom are: 1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0.20 to 0.40 per cent. It would have been most remarkable if that point had been over-

looked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's, and in three cases by my method. The results were :

Lunge's Method.	Gladding's Method.
50.59 per cent.	50.60 per cent.
50.63 " "	50.66 " "
50.56 " "	....
<hr/>	<hr/>
Average, 50.59 " "	Average, 50.63 " "

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times, exactly in the way described by me ; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless, when observing the precautions in washing, pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e. g.*; in a hole made in asbestos cardboard), dissolving in water and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding ; but I rejected

it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been ; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were :

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid)		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49.64	0.60	50.24	48.98	1.03	50.01
49.36	1.01	50.37	48.84	1.39	50.23
49.07	1.21	50.28	49.02	1.07	50.19
49.25	1.04	50.29	49.30	0.73	50.03
<hr/>			<hr/>		
Average,		50.29	Average,		50.09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0.20 per cent.) ; with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be: That in most points Gladding's method is correct, but in *not a single case* more so than my method ; his modifications can not be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide ; on the contrary this is very easy to avoid. If it has, after all, happened by incorrect manip-

ulation, Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-makers' Handbook."

In conclusion I would add that I have also tried the method recommended by F. Johnson (*Chem. News*, 1894, 70, 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

## IMPROVEMENT IN THE MANUFACTURE OF ACETONE.<sup>1</sup>

By E. R. SQUIBB, M.D.

Received January 17, 1895.

THE increasing use of acetone as a chemical solvent, and especially the relation of acetone to the manufacture of chloroform, gives importance to any improvement in its production.

Up to this time the writer knows of no process of manufacture except by the destructive distillation of acetates at high temperature. The acetates are charged into stills and heated as long as they yield any acetone. Then the acetates being decomposed to waste carbonates are discharged and the stills recharged with fresh acetate, making an interrupted process of repeated charging and discharging and heating and cooling. This process is very old; but two patents have been taken out in this country on some details of the process and apparatus.

The writer proposed to himself to make acetone directly from acetic acid by a continuous process, and has accomplished that object.

In Gmelin's Handbook of Chemistry, Cavendish Society edition, 1853, 8, 291, under the head of decomposition of acetic acid by heat, much work is given where the vapor of acetic acid was

<sup>1</sup> Read before the N. Y. Section, January 11, 1895.

passed through heated tubes, acetone being one of the products; and, on this line of investigation, the writer's work was taken up.

It was not difficult to see that the discrepant results reached by the authorities were due to differing physical conditions, and different degrees of heating, since it was mechanically quite certain that a current of vapor passing through a stationary tube, heated from below, whether empty or filled, could not be heated to the same degree in all parts of the tube, and therefore could not give the same decomposition in all parts.

The work undertaken was commenced in very long-necked glass bulbs, held in a horizontal position, so that they might be stationary or be revolved by hand, and these were heated by a bath of Wood's metal—the acid being passed in, and the products coming out through horizontal tubes in the long necks.

Experiences with these bulbs led to much better mechanical devices. A small flask was arranged as a still, and from this, by a gas-burner, a constant current of acetic acid vapor could be produced at any desired rate. The rate was regulated by the rate of supply of liquid acid from an elevated graduated supply vessel, the supply going to the still through a glass tube, in which the rate of dropping was seen and controlled by a stop-cock. Then, by varying the acid supply and the heat from the burner, the boiling liquid in the still could be kept at about a constant level, and with a controllable known rate of vapor supply.

At some distance from this end of this apparatus the condensing apparatus was arranged to receive the distillates. The products of distillation were first received in a flask where most of the watery vapor and undecomposed acid was condensed, but where the temperature continued so high that but a mere trace of acetone was arrested there. From the neck of this flask the remaining gases and vapors passed through a good condenser, which delivered the remainder of the water and undecomposed acid and the acetone into a flask immersed in an ice-bath. Here almost all the condensible vapors were condensed. The gases and uncondensed vapors were taken from the neck of this flask to a small wash-bottle supplied with water, by which the current of gases was washed. Here waste acetone enough was caught to increase the volume of contents to a point at which all went off



together in the current of gases, and the level remained constant. Next was a wash-bottle containing a strong solution of sodium hydroxide. Through this the residual gases were passed in order that most of the carbon dioxide might be combined. Finally, the gases were passed through another small wash-bottle containing water. At the small exit tube of this bottle the gases were tested for inflammability, and the proportion of methane and carbon monoxide was estimated by the absence or the degree of inflammability. Except at the times of testing, this exit tube was connected to a Sprengel water-pump, and a minus pressure of one to six cm. of mercury was maintained on the entire apparatus. This served to relieve all joints and connections and caused all the leakages to be inward, whilst a mercury-gauge at each end gave due notice of obstruction or irregularities.

These two ends of the apparatus remaining constant, the intervening space was occupied by the varying form of distilling or decomposing apparatus. An earthenware drain-pipe, with movable tile ends served as a furnace. This drain-pipe, supported in a horizontal position, had six holes drilled above and below. Each lower hole was large enough to admit a Bunsen burner with limited air space around it, while the holes on top, to give exit to the products of the combustion were smaller. The decomposing tubes or stills of wrought iron, with cast iron ends, occupied this drain-pipe furnace, being connected with the vapor supply apparatus at one end and the condenser at the other.

Much preliminary work was necessary in getting the apparatus in good working order, and in following up tangential points, but these are passed over, and only the important work given—and that not always in the order in which it was done, but in an order which brings the results into a more logical sequence more easily understood.

Two strengths of acetic acid were used. First, an acid containing thirty-six per cent. of absolute acid. But as this gave distillates unnecessarily dilute it was generally given up in favor of a sixty per cent. acid, although the reactions were not noticeably different in the use of the two strengths. Hence with two exceptions the results given are from a sixty per cent. acetic acid.

Reducing the work from the disorderly way in which it was done to a natural order, and rejecting what was not trustworthy, it is best to begin with some repetitions of work already long on record. (See Gmelin's Handbook, and other authorities.)

A tube of wrought iron about thirty-six cm. (fourteen inches) in length by six and five-tenths cm. (two and five-tenths inches) internal diameter, reduced at each end to tubing of about six-tenths cm. (one-fourth inch), was held stationary in the center of the furnace, and connected at one end with the acid vapor supply and at the other with the condensers. This tube could be heated by the gas-burners to any desired degree up to a dull red heat. The trials were made under as nearly the same conditions as practicable, the running time being about three and five-tenths hours, and under close observation. The amount of sixty per cent. acetic acid which could be passed in, in vapor during this time, varied much—generally 250 to 350 cc. The quantities used were always reduced to absolute acid ( $\text{HC}_2\text{H}_3\text{O}_2$ , = 59.86), and the results are given in the same acid, but a high degree of accuracy was impracticable, and therefore not aimed at.

(1) With the tube empty and heated nearly to redness at first, and finally to a dull red heat, 290 cc. of sixty per cent. acid = 174 grams absolute acid, was passed in in three and five-tenths hours. About 111 grams of this acid passed through unchanged, and sixty-three grams were decomposed. That is, about 63.8 per cent. came through unchanged, and 36.2 per cent. were decomposed. In the first receiving flask, kept hot by the vapor, there was no acetone, but only 132 cc. of a fifty-three per cent. acid. In the second flask, in the ice-bath, there was 115 cc. of a thirty-six per cent. acid; and this liquid, roughly estimated by the iodoform test, contained ten to twelve per cent. of acetone. From the final wash-bottle came a stream of inflammable gas—probably methane and carbon monoxide—that would burn almost continuously.

(2) Next, this stationary tube was filled with coarsely granulated pumice-stone, freed from large pieces and from dust, and so tightly packed as to have spring enough to keep the tube full when expanded by heating. Into this, in three and five-tenths

hours, 189 grams of absolute acid, in vapor, were passed, and yielded in the first, hot flask 103 cc. of fifty-four per cent. acid = 55.62 grams absolute acid. In the second, ice-bath flask 138 cc. of 38.4 per cent. acid = 52.97 grams of absolute acid, making 108.6 grams out of 189 grams distilled over unchanged, and 80.4 grams decomposed. The contents of this second flask were about 14.5 per cent. acetone. The stream of inflammable gases was estimated as being not less but rather greater than with the empty tube.

(3) Next, took the pumice from the tube, divided it into two parts, and rejecting one-half, intimately mixed with the other half 500 grams of dry, precipitated barium carbonate. Charged the tube with this mixture, having a little unmixed pumice at both ends. Barium carbonate was selected to multiply surface, as being a rather heavy powder that would not shrink nor fuse, nor be likely to decompose.

About 450 cc. of sixty per cent. acid = 270 grams of absolute acid were passed, in vapor, in three and five-tenths hours, into this mixture, heated as before. The distillate in the first, hot flask was eighty-one cc. of acid water of only one and six-tenths per cent. = one and three-tenths grams absolute acid. In the second ice-bath flask was 227 cc. sp. gr. about 0.955, containing one and two-tenths per cent. acid = two and seven-tenths grams absolute acid. Of the 270 grams passed in, four grams only distilled over unchanged, while 266 grams were decomposed. The 227 cc. of distillate in the second flask contained about 23.3 per cent. of acetone. This proportion gives about twenty per cent. of acetone from the 266 grams of absolute acid used. The stream of inflammable gases was very much greater than in the other experiments, burning with an almost continuous large flame.

The desired splitting of acetic acid to yield acetone requires two molecules of the acid to yield one molecule of acetone, the residuary products being one molecule each of carbon dioxide and water. That is, 120 grams of absolute acetic acid should give

58	grams of acetone,
44	“ “ carbon dioxide,
18	“ “ water, or

by percentage the acid should give

48.33	per cent.	acetone,
36.67	"	carbon dioxide,
15.00	"	water.

When marsh-gas or methane ( $\text{CH}_4$ ) and carbon monoxide ( $\text{CO}$ ) are formed it is probably largely, if not entirely, through a secondary decomposition of the acetone by a higher heat than that which gives the primary decomposition into acetone, carbon dioxide, and water, and when acetone and methane are produced together, it is rational to suppose that inequalities of heating are the cause. That is, if acetone be produced it indicates that the exact conditions required are present at that time and place. Then it follows that if these exact conditions be extended throughout the whole time and place of reaction the acetone splitting of the acid only can occur, and no methane or other products of other reactions can be produced. The conditions for producing these different reactions are doubtless different degrees of heating, and uniformity of reaction can be expected only from uniformity of heating. And the differences in the degrees of heat required to produce the different reactions here, do not seem to be great.

The physical and mechanical conditions of heating a stationary tube can not possibly yield an equal degree of heating to the contents of such a tube, especially where only a part of such contents is in motion. Even if the whole outside of the tube could be equally heated—as it could not be practically—the contents would be cooler from circumference to center. But in this case, where a current of vapor at about  $100^\circ \text{C}$ . is passed continually, into a tube the outside of which is kept unequally heated to  $500^\circ$  or  $600^\circ \text{C}$ ., and where this current has to find its way at varying speed through varying friction and expansion, only a varying decomposition can be possible, and the conclusion must be that if uniform decomposition is to be reached it must be through uniform conditions.

Equable heating in a stationary tube, under the conditions of this process, being impracticable, it became necessary to devise some better form of still; and a careful consideration of the principles involved, and the especial mechanical difficulties of this

decomposition, led the writer to a form of rotary still, which, after some alterations and modifications, has proved successful.

A wrought-iron tube about thirty-six cm. (fourteen inches) long by 12.7 cm. (five inches) in diameter, contracted at the ends to central hollow journals of about two cm. (three-fourths inch) external diameter and one and two-tenths cm. (five-tenths inch) bore, free to revolve, was supported in the center of the eighteen cm. (seven inches) drain-pipe furnace and connected at one end with the vapor supply and the other with the condensers by air-tight glands or "stuffing-boxes." The ends were provided with charging and discharging openings which could be closed air-tight, and the still was revolved slowly by means of a pulley on one end of the hollow shaft. A small stationary tube passed into the still through the revolving shaft to convey the acid vapor to the entrance of the still at one end, and a similar tube gave exit to the products of the decomposition at the other, condenser end. It was necessary to protect this tube from obstruction by dust carried by the current of vapors, and this was done by a cartridge of rolled up, wire cloth, filled with glass wool. This rotary still was driven at the rate of three to six revolutions per minute by a small water-motor, and was found to heat with great equability as it revolved over the burners. Inside of the still, at equal distances apart on the periphery, five L-shaped, longitudinal strips of sheet iron were riveted. These were necessary to prevent the charge from sliding round as the iron became smooth, and they were found to carry the charge round, turn it over, and mix it most effectively at each revolution. Thus, while by the revolutions over the source of heating the shell was heated very uniformly, this continuous moving and turning over of the contents must bring all parts of the charge, solids and vapors alike, in successive contact with the hot surfaces and the cooler atmosphere of the still, and thus secure a fair degree of equable heating. The still being about one-third filled with the solid charge and slowly rotated, the charge occupies principally,—not the bottom of the still directly over the fire, but the ascending third which has just been over the fire. Then, as the charge is carried up, the superficial cooler portion, too deep to be held by the longitudinal shelves, slides back upon the hot surface below,

while the portion carried on by the shelves falls back, shelf by shelf, from contact with the hot shell through the atmosphere of vapor, upon the cooler portions below to be mixed and carried up again in a similar order. At the same time the whole atmosphere of the still is filled with dust which becomes very fine, and very largely multiplies the surfaces of contact with the vapor, for decomposition, whilst the vapors pass slowly and uniformly and with a minimum of friction to the exit at the condenser end. If the motion and heating of a charge in this still be compared with those in a stationary still with a horizontal stirrer driven by a vertical shaft, the advantages of the former will be easily understood. The latter moves the charge round over the fire, but has a comparatively slight effect in bringing new portions of the charge successively in contact with the heating surfaces, and it does not tend to prevent horizontal stratification of the charge with consequent irregular heating; and it does not tend to the fullest contact of the vapors with the surfaces of the charge, where the decomposition probably takes place. After the inevitable number of trials and adjustments and breakings down, the following successful experiments are selected from a large number.

(4) As a parallel experiment to (1) with the stationary still, the rotary still was used empty.

About 200 cc. of thirty-six per cent. acid = seventy-two grams of absolute acid was slowly passed into the heated, rotating, empty still.

The first hot flask of distillate contained thirty-three cc. of acid of 14.6 per cent. = 4.82 grams absolute acid.

The second ice-bath flask contained 142 cc. of acid acetone 12.6 per cent. = 17.89 grams absolute acid. Then  $4.82 + 17.89 = 22.71$  grams absolute acid distilled over unchanged. Then seventy-two grams —  $22.71 = 49.29$  grams of acid decomposed. The second distillate gave an estimate of 12.1 grams acetone. Then as  $49.29$  acid :  $12.1$  acetone ::  $100 : 24.5$  per cent. acetone from the acid. The current of inflammable gas was considerable, but less than in (1).

(5) The rotary still was charged with about a liter of the same granulated pumice used in (2), and when heated about 295 cc.

of sixty per cent. acid = 177 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate, hot flask, had 108 cc. of acid water of four and four-tenths per cent. = 4.75 grams acid.

The second distillate, ice-bath flask, had 116 cc. acid acetone two and four-tenths per cent. acid = 2.78 grams acid.

Then  $4.75 + 2.78 = 7.53$  grams acid came over unchanged, out of 177 grams passed in; or,  $177 - 7.53 = 169.47$  grams decomposed.

The acetone estimated by iodoform was 24.3 per cent. of the acid decomposed.

(6) About 500 grams of precipitated barium carbonate was put into the rotary still on top of the charge of pumice, and when the whole was heated, 380 cc. sixty per cent. acid = 288 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate was 108 cc. of acid water containing three and nine-tenths grams acid.

The second distillate was 135 cc. of acid acetone containing two and seven-tenths grams acid.

228 grams acid — six and six-tenths grams over unchanged = 221.4 grams decomposed.

The estimated acetone was sixteen per cent. of the acid decomposed.

Much inflammable gas throughout the process.

(7) About 456 grams of precipitated barium carbonate put into the cleaned-out rotary still, and when heated 510 cc. of thirty-six per cent. acid = 183.6 grams absolute acid was passed in, in four and five-tenths hours. About 24.5 grams of acid came over unchanged, leaving 159.1 grams, decomposed.

The acetone was estimated at 53.7 grams, or about thirty-four per cent. of the decomposed acid.

(8) Charged the rotary still with 1000 grams of dry barium acetate and distilled this acetate as long as it would yield a distillate, and until it was reduced to 770 grams of barium carbonate quite free from acetate. This yielded acetone estimated by iodoform at about sixty per cent of the theoretical quantity.

When the distillation from the acetate had ceased the receivers were changed and 490 cc. of sixty per cent. acid = 294 grams

of absolute acid were passed into this charge of carbonate in about four and five-tenths hours.

The distillate was received in five fractions.

1st.	37 cc. of acid water containing 15.6 per cent. acid or	5.77 grams.	.
2nd.	256 " " dilute acetone " 4.4 " " " " "	11.26	"
3rd.	230 " " " " " 9.6 " " " " "	22.08	"
4th.	46 " " " " " 11.0 " " " " "	5.06	"
5th.	26 " " " " " 17.6 " " " " "	4.58	"

595 cc.

Distilled over undecomposed, 48.75 grams.

294 grams—forty-nine grams = 245 grams decomposed.

In each of the second and third flasks was about forty cc. of water at the start. Then eighty from 595 gave 515 cc. of total distillate from the 490 cc. fed in.

Acetate required from 245 grams acid 118 grams. Estimated yield seventy-one gram or sixty per cent. of the required yield.

On the following day, without having opened the still, it was reheated and 530 cc. of sixty per cent. acid = 318 grams of absolute acid was passed in, in vapor. From low street pressure in the gas-mains the heat on this day was deficient.

1st distillate	50 cc. acid water containing 19.6 per cent. acid or.	9.8 grams.
2d	" 255 " dilute acetone " 10.0 " " " " "	25.5 "
3d	" 138 " " " " 6.0 " " " " "	8.3 "

443 cc.

43.6 grams.

318 grams—forty-four grams = 274 grams acid decomposed.

Acetone required from 274 grams acid 132 grams. Estimated yield ninety-five grams or seventy-two per cent. of the required yield.

On the day following, again without opening the still, in about four hours, passed in 535 cc. of sixty per cent. acid = 321 grams of absolute acid.

1st dis., hot flask,	22 cc. acid water containing 7.6 per cent. acid or	1.67 gms.
2d	" ice-bath, 258 " dilute acetone " 4.8 " " " " "	12.38 "
3d	" " 131 " " " " 7.6 " " " " "	9.96 "

411 cc.

24.01 gms.

321 grams—twenty-four grams = 297 grams acid decomposed.



Acetone required by theory from 296 grams acid 143 grams. Obtained by estimate about 113 grams or nearly eighty per cent. of the required yield.

Now, upon cooling and opening the still, samples taken from various parts of the contents were all found to be barium carbonate and free from acetic acid.

During the progress of these distillations from pumice stone, from carbonates, and from the empty stills alike, whenever the supply of acid vapor was cut off the distillation almost instantly ceased, showing that there was then nothing in the still to decompose.

This, then, is the improved, continuous process for the production of acetone directly from acetic acid, which avoids and saves the intermediate steps of forming and decomposing acetates.

The formation of acetates in the still was repeatedly tried with both barium and calcium carbonates, but always failed until the temperature was reduced to about the boiling-point of water, or the condensing-point of watery vapor, and then the acetates formed, cohered and adhered to the ribs and shell of the still, and no longer moved until again decomposed by a higher heat.

Corresponding trials were made with calcium carbonate and with calcium acetate decomposed to carbonate, with results very similar to those above given, but the barium carbonate seemed to answer best, possibly because it yields a heavier powder that occupies less space and moves better.

When commercial calcium acetate was used, tarry matters obstructed the exit tubes and contaminated the distillates. The portion of these tarry matters that was reduced to charcoal in the still, and there mixed with the carbonate, seemed to be rather beneficial than obstructive. But on the whole the process appeared to do better with carbonates reduced from acetates that were made for the purpose from good materials. As the process seems to be rather a mechanical or physical one of surface contact, it would be reasonable to expect better results from reduced carbonates than from precipitated carbonates. And it is still an open question whether, on the large manufacturing

scale, with better control of the essentials, heat and motion, pumice or bone black, or some other such substance, will not be better than the carbonates. Of one thing the writer is quite convinced, and that is that the close regulation of the heating within narrow limits of variation, is far the most important element in the process. Within very narrow limits, too little heat gives undecomposed acid, while too much gives inflammable gases in place of acetone. But on the large scale this element will be under much better control, whilst a proportionately longer still will give the acid vapor farther to go and a prolonged exposure to the limited heating and contact.

There are no patents sought for on this process or apparatus.

The dilute acetone from this process is fairly good and clean, and is colorless except for the action of the free acid contained on the iron tubing. With the free acid the specific gravity by hydrometer varies between 0.93 and 0.97. No part of the distillate has more than a thin film of oil on the surface too small to be measured, and this oily surface is only in the first flask with the acid water. On further dilution of the ice-bath distillate it is rendered opalescent for a minute or two and then becomes again transparent.

This distillate (undiluted) is a good solvent for many substances, and is probably pure enough for the manufacture of chloroform.

When allowed to stand some days upon caustic lime and then poured off and rectified, it is much improved in character and strength, and is then adapted to a still larger number of uses, and is perhaps better adapted to the manufacture of chloroform.

The product of this first rectification was then digested with about ten per cent. of dry calcium chloride. This abstracted most of the water and settled in dense solution at the bottom of the bright yellowish acetone. This latter was separated and distilled, and again digested for several days with ten per cent. of fresh calcium chloride, being frequently well shaken. Again twice separated and distilled from fresh portions of calcium chloride, in a capacious flask with a good Hempel tube filled with small glass marbles, and the whole apparatus filled with well-dried air, and distilled directly into specific gravity bottles, such as are described in the *Ephemeris*, 4, 1448—it gave six

fractions, four of which had the specific gravities at  $1\frac{5}{8}^{\circ}$  C., as follows: First, 0.79662; second, 0.79704; third, 0.79712; sixth, 0.79793. The irregularities of these differences are doubtless due to differences in rate of boiling, yet they demonstrate conclusively that the first fraction can not be anhydrous.

Authorities differ much as to the specific gravity of acetone. The lowest noticed is, given by W. H. Perkin, Ph.D., F. R. S., in the *J. Chem. Soc.*, 1884, 45, 478. He gives the specific gravity at  $1\frac{5}{8}^{\circ}$  as 0.79652, and at  $2\frac{5}{8}^{\circ}$  as 0.78669—and says this is lower than that usually observed, but agrees pretty closely with that of Linnemann, who obtained  $1\frac{5}{8}^{\circ}$  = 0.7975. Thorpe's number, calculated for this temperature, gave  $1\frac{5}{8}^{\circ}$  = 0.80244. Judging from the circumstance that the writer's fractions did not agree, and that therefore there was no constant boiling-point to his distillate, and hence no part anhydrous—his and Perkin's results are both too high.

Notwithstanding this, the writer accepts, for the present at least, his own result as a basis for the following specific gravities of dilutions. His best results as obtained by the use of his above-mentioned specific gravity bottles, and a sensitive thermometer in tenths of a degree, recently compared with a standard, are as follows:

At  $4^{\circ}$  C. 0.808157. At  $1\frac{5}{8}^{\circ}$  C. 0.796620. At  $2\frac{5}{8}^{\circ}$  C. 0.786988.

It was first desirable to know whether dilutions of acetone with water were mere mixtures, or whether as in the case of alcohol there was molecular combination with contraction and elevation of temperature. It was found that when forty cc. of acetone of about ninety per cent. was mixed with forty cc. of water there was a contraction of three and two-tenths cc., and an increase of temperature of  $5.6^{\circ}$  C., with an effervescence of gas as in alcohol.

The proportion of ten grams of recently boiled distilled water added to ninety grams of this distillate, mixed by connecting two flasks with the weighed quantities, and passing the liquids back and forth without exposure to external air or loss of vapor, gave the following specific gravities:

Acetone at  $4^{\circ}$  C. 0.8371.  $1\frac{5}{8}^{\circ}$  C. 0.8260.  $2\frac{5}{8}^{\circ}$  C. 0.8168 for ten per cent. of water, or ninety per cent. acetone.

This method of dilution by weighing the acetone and water separately in flasks and then connecting the flasks for mixing without loss of vapor or outer air contact was adopted for the basis of the following Acetone Table. The lines of the table that are given in heavy-faced type are given from actual observation, and the remainder by interpolation.

Acetone =  $C_2H_4O$ , or dimethyl ketone =  $CH_3COCH_3$ , is a transparent, colorless, mobile, light, inflammable liquid of an agreeable spirituous or ethereal odor, with a suggestion of mint, and a sharp, biting taste. The suggestion of mint in the odor varies in strength in different samples, and probably does not belong to acetone, but comes from a minute trace of impurity. It boils at  $56.3^\circ C.$  (Regnault). The specific gravity when very nearly anhydrous is at  $\frac{4}{4}^\circ C.$  0.808157, at  $\frac{15}{15}^\circ C.$  0.796620, at  $\frac{25}{25}^\circ C.$  0.786988. It mixes in all proportions with alcohol and water, and is a very general solvent, dissolving many substances that are insoluble in alcohol.

## ACETONE TABLE.

The lines of figures in broad-faced type are given from actual observation. The remainder of the table is interpolated.

The Acetone assumed for the basis of the table was not absolutely anhydrous, though probably very nearly so.

In the percentages no account is taken of the weight of the gases liberated on mixing acetone with water.

SPECIFIC GRAVITY AT			Percent- age by weight.	SPECIFIC GRAVITY AT			Percent- age by weight.
$\frac{4}{4}^\circ C.$	$\frac{15}{15}^\circ C.$	$\frac{25}{25}^\circ C.$		$\frac{4}{4}^\circ C.$	$\frac{15}{15}^\circ C.$	$\frac{25}{25}^\circ C.$	
0.8082	0.7966	0.7870	100	0.8524	0.8425	0.8338	84
0.8111	0.7995	0.7900	99	0.8549	0.8453	0.8366	83
0.8139	0.8025	0.7930	98	0.8575	0.8481	0.8394	82
0.8168	0.8054	0.7959	97	0.8600	0.8508	0.8422	81
0.8197	0.8084	0.7989	96	0.8626	0.8536	0.8450	80
0.8226	0.8113	0.8019	95	0.8651	0.8561	0.8476	79
0.8255	0.8142	0.8049	94	0.8676	0.8587	0.8502	78
0.8284	0.8172	0.8079	93	0.8701	0.8612	0.8528	77
0.8313	0.8201	0.8109	92	0.8726	0.8637	0.8554	76
0.8342	0.8231	0.8138	91	0.8752	0.8663	0.8580	75
0.8371	0.8260	0.8168	90	0.8777	0.8688	0.8605	74
0.8397	0.8288	0.8196	89	0.8802	0.8714	0.8631	73
0.8422	0.8315	0.8225	88	0.8827	0.8739	0.8657	72
0.8448	0.8343	0.8253	87	0.8852	0.8764	0.8683	71
0.8473	0.8370	0.8281	86	0.8877	0.8790	0.8709	70
0.8498	0.8398	0.8309	85	0.8900	0.8813	0.8732	69

SPECIFIC GRAVITY AT			Percent- age by weight.	SPECIFIC GRAVITY AT			Percent- age by weight.
$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.		$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.	
0.8923	0.8836	0.8756	68	0.9469	0.9392	0.9332	43
0.8946	0.8858	0.8779	67	0.9489	0.9412	0.9353	42
0.8969	0.8881	0.8803	66	0.9508	0.9433	0.9375	41
0.8992	0.8904	0.8826	65	0.9527	0.9454	0.9397	40
0.9014	0.8927	0.8850	64	0.9541	0.9469	0.9413	39
0.9037	0.8950	0.8874	63	0.9554	0.9484	0.9430	38
0.9060	0.8973	0.8897	62	0.9567	0.9499	0.9446	37
0.9083	0.8996	0.8921	61	0.9580	0.9514	0.9462	36
0.9106	0.9019	0.8944	60	0.9594	0.9529	0.9479	35
0.9129	0.9041	0.8968	59	0.9607	0.9544	0.9495	34
0.9151	0.9064	0.8991	58	0.9620	0.9559	0.9512	33
0.9174	0.9087	0.9015	57	0.9634	0.9574	0.9528	32
0.9197	0.9110	0.9038	56	0.9647	0.9589	0.9545	31
0.9220	0.9133	0.9062	55	0.9660	0.9604	0.9561	30
0.9243	0.9156	0.9086	54	0.9674	0.9619	0.9578	29
0.9266	0.9179	0.9109	53	0.9687	0.9635	0.9594	28
0.9289	0.9202	0.9133	52	0.9700	0.9650	0.9611	27
0.9311	0.9224	0.9156	51	0.9714	0.9665	0.9627	26
0.9334	0.9247	0.9180	50	0.9727	0.9680	0.9644	25
0.9354	0.9268	0.9202	49	0.9740	0.9795	0.9660	24
0.9373	0.9289	0.9223	48	0.9754	0.9710	0.9677	23
0.9392	0.9309	0.9245	47	0.9767	0.9725	0.9693	22
0.9411	0.9330	0.9267	46	0.9780	0.9740	0.9709	21
0.9431	0.9351	0.9288	45	0.9794	0.9755	0.9726	20
0.9450	0.9371	0.9310	44				

## REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.<sup>1</sup>

BY F. W. CLARKE.

Received January 2, 1895.

*To the Members of the American Chemical Society:*

YOUR committee upon atomic weights respectfully submits the following report, which summarizes the work done in this department of chemistry during 1894. Although the volume of completed determinations is not large, it is known that several important investigations are in progress, from which valuable results may be expected in the near future. It is in this country that the greatest activity exists, and that the greatest progress is being made at present; and the preparation of these reports is therefore a peculiarly appropriate function of the Society. The data for 1894 are as follows:

*The H: O ratio.*—An interesting attempt at the indirect measurement of this ratio, which is the base line upon which our sys-

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

tem of atomic weights depends, has been made by Julius Thomsen.<sup>1</sup> His determinations are really determinations of the ratio  $\text{NH}_3 : \text{HCl}$ , and were conducted thus: First, pure, dry, gaseous hydrochloric acid was passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, gaseous ammonia was passed through to slight excess, and the apparatus was weighed again. The excess of ammonia was then measured by titration with standard hydrochloric acid. In weighing, the apparatus was tared by another as nearly like it as possible, containing the same amount of water. Three sets of weighings were made, with apparatus of different size, and these Thomsen considers separately, giving the greatest weight to the experiments involving the largest masses of material. The data are as follows, with the ratio  $\frac{\text{HCl}}{\text{NH}_3}$  in the third column:

## FIRST SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio
5.1624	2.4120	2.1403
3.9425	1.8409	2.1416
4.6544	2.1739	2.1411
3.9840	1.8609	2.1409
5.3295	2.4898	2.1406
4.2517	1.9863	2.1405
4.8287	2.2550	2.1414
6.4377	3.0068	2.1411
4.1804	1.9528	2.1407
5.0363	2.3523	2.1410
4.6408	2.1685	2.1411

## SECOND SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio.
11.8418	5.5302	2.14130
14.3018	6.6808	2.14073
12.1502	5.6759	2.14067
11.5443	5.3927	2.14073
12.3617	5.7733	2.14118

## THIRD SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio.
19.3455	9.0360	2.14094
19.4578	9.0890	2.14081

<sup>1</sup>*Ztschr. phys. Chem.*, 13, 398.

From the sums of the weights Thomsen finds the ratio to be 2.14087, or 2.13934 in vacuo. From this, using Ostwald's reduction of Stas' data for the atomic weights of nitrogen and chlorine, he gets the ratio  $O : H :: 16 : 0.99946$ , or almost exactly  $16 : 1$ . In a later paper<sup>1</sup> Thomsen himself recalculates Stas' data, with  $O = 16$  as the basis of computation, and derives from them the subjoined values for the elements which Stas studied :

Ag.....	107.9299
Cl .....	35.4494
Br .....	79.9510
I .....	126.8556
S .....	32.0606
Pb.....	206.9042
K .....	39.1507
Na.....	23.0543
Li .....	7.0307
N .....	14.0396

Combining these values for chlorine and nitrogen with his ratio  $HCl : NH_3$ , he gets  $O : H :: 16 : 0.9992$ . This, however, is only an apparent support of Prout's hypothesis, for it depends upon the anti-Proutian determinations of Stas. If we calculate from Thomsen's new ratio with  $N = 14$  and  $Cl = 35.5$ , it gives  $H = 1.0242$ ; which is most unsatisfactory. In short, the method followed by Thomsen is too indirect and subject to too many possibilities of error to entitle it to much weight in fixing so important a constant as the atomic weight of oxygen. The direct processes, followed by several recent investigators, and giving  $O = 15.87$  to  $15.89$  are much more trustworthy. Meyer and Seubert<sup>2</sup>, in their criticism of Thomsen's work, have pointed out some of its uncertainties.

In this connection it may be noted that Scott's research upon the composition of water by volume, cited by abstract in the report of last year, has been published in full in the *Philosophical Transactions*.<sup>3</sup>

*Strontium*.—The atomic weight of strontium has been re-determined by Richards<sup>4</sup> from analyses of the bromide. The first ratio measured, after a careful preliminary study of materials

<sup>1</sup> *Ztschr. phys. Chem.*, 13, 726.

<sup>2</sup> *Ber d. chem. Ges.*, 27, 2770. See also abstract by Ostwald in *Ztschr. phys. Chem.*, 15, 705.

<sup>3</sup> 184, 543, 1893.

<sup>4</sup> *Proc. Amer. Acad.* 1894, 369.

and methods, was that between silver and strontium bromide. Of this ratio, three sets of determinations were made, all volumetric, but with differences of detail in the process. The weights are as follows, with the ratio  $\text{Ag}_2:\text{SrBr}_2::100:x$  in the third column:

FIRST SERIES.		
Wt. Ag.	Wt. $\text{SrBr}_2$ .	Ratio.
1.30755	1.49962	114.689
2.10351	2.41225	114.677
2.23357	2.56153	114.683
5.36840	6.15663	114.683
<hr/>		
Sum, 11.01393	12.63003	114.683

SECOND SERIES.		
Wt. Ag.	Wt. $\text{SrBr}_2$ .	Ratio.
1.30762	1.49962	114.683
2.10322	2.41225	114.693
4.57502	5.24727	114.694
5.36800	6.15663	114.691
<hr/>		
Sum, 13.35386	15.31577	114.692

THIRD SERIES.		
Wt. Ag.	Wt. $\text{SrBr}_2$ .	Ratio.
2.5434	2.9172	114.697
3.3957	3.8946	114.692
3.9607	4.5426	114.692
4.5750	5.2473	114.695
<hr/>		
Sum, 14.4748	16.6017	114.694

From these data we have, if  $\text{Ag} = 107.93$ , and  $\text{Br} = 79.955$ , ( $\text{O} = 16$ ), the following results:

From first series.....	$\text{Sr} = 87.644$
" second series.....	87.663
" third series.....	87.668

In two additional series, partly identical with the foregoing, the silver bromide thrown down was collected and weighed. I subjoin the weighings with the ratio  $2\text{AgBr}:\text{SrBr}_2$ , in the last column.

FIRST SERIES.		
$2\text{AgBr}$ .	$\text{SrBr}_2$ .	Ratio.
2.4415	1.6086	65.886
2.8561	1.8817	65.884
6.9337	4.5681	65.883
<hr/>		
Sum, 12.2313	8.0584	65.884



## SECOND SERIES.

2AgBr.	SrBr <sub>2</sub> .	Ratio.
2.27625	1.49962	65.881
3.66140	2.41225	65.883
3.88776	2.56153	65.887
9.34497	6.15663	65.882
<hr/>		
Sum, 19.17038	12.63003	65.883

From the first series..... Sr=87.660

" " second series..... 87.659

The average of all five series is Sr=87.659.

*Barium*.—Richards has corroborated his earlier determinations of the atomic weight of barium, which were made with the bromide, by means of additional series of experiments upon the chloride.<sup>1</sup> The work was carried out in the most elaborate and thorough manner, and for details the original paper must be consulted. First, barium chloride was titrated with standard solutions of silver, and the several series represent different methods of ascertaining accurately the end point. The data are as follows, with the ratio Ag, : BaCl<sub>2</sub> :: 100 : x in the third column.

## FIRST SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.507
0.7199	0.6950	96.541

Mean, 96.512

## SECOND SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.59993	6.36974	96.512
5.55229	5.36010	96.539
4.06380	3.92244	96.522

Mean, 96.524

## THIRD SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
4.4355	4.2815	96.528
2.7440	2.6488	96.531
6.1865	5.9712	96.520
3.4023	3.2841	96.526

Mean, 96.526

<sup>1</sup> *Proc. Amer. Acad.*, 29, 55.

## FOURTH SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.7342	6.50022	96.525
10.6023	10.23365	96.523

Mean, 96.524

All the weights represent vacuum standards. From the four series the atomic weight of barium is deduced as follows; when  $O = 16$ .

First series .....	Ba = 137.419
Second " .....	" 137.445
Third " .....	" 137.449
Fourth " .....	" 137.445

In three more series of experiments Richards determined the ratio between  $2AgCl$  and  $BaCl_2$ . The data are subjoined, with the ratio  $2AgCl : BaCl_2 :: 100 : x$  appended.

## FIRST SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
8.7673	6.3697	72.653
5.1979	3.7765	72.654
4.9342	3.5846	72.648
2.0765	1.5085	72.646
4.4271	3.2163	72.650

Mean, 72.649

## SECOND SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
2.09750	1.52384	72.650
7.37610	5.36010	72.669
5.39906	3.92244	72.650

Mean, 72.6563

## THIRD SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
8.2189	5.97123	72.6524
4.5199	3.28410	72.6587

Mean, 72.6555

Hence we have for Ba,

First series .....	Ba = 137.428
Second " .....	" = 137.446
Third " .....	" = 137.444

The mean of all is 137.440, as against 137.434 found in the work on the bromide. By combining the two chloride ratios,

Ag: BaCl, and 2AgCl: BaCl, the ratio Ag: Cl can be computed. This gives  $\text{Ag} = 107.930$ , a value identical with that of Stas.

*Cobalt and Nickel.*—The atomic weights of these two metals have been redetermined by Winkler,<sup>1</sup> who adopts a radically new method, using the pure electrolytic elements as a starting-point. In each case, the weighed metal, deposited upon platinum, is treated with a weighed excess of iodine dissolved in potassium iodide. The metals are thus converted into iodides, and the excess of iodine is then measured by titration with thio-sulphate solution. Thus the direct ratios, Co: I, Ni: I, are determined. Two series of estimations are given for each metal, with results as follows. The atomic weights used in calculation are  $\text{H} = 1$ ,  $\text{I} = 126.53$ .

## FIRST SERIES—COBALT.

Wt. Co.	Wt. I.	At. Wt. Co.
0.4999	2.128837	59.4242
0.5084	2.166750	59.3772
0.5290	2.254335	59.3828
0.6822	2.908399	59.3582
0.6715	2.861617	59.3824

Mean, 59.3849

## SECOND SERIES—COBALT.

Wt. Co.	Wt. I.	At. Wt. Co.
0.5185	2.209694	59.3798
0.5267	2.246037	59.3430
0.5319	2.268736	59.3294

Mean, 59.3507

Mean of all, Co = 59.3678.

## FIRST SERIES—NICKEL.

Wt. Ni.	Wt. I.	At. Wt. Ni.
0.5144	2.217494	58.6702
0.4983	2.148502	58.6918
0.5265	2.268742	58.7268
0.6889	2.970709	58.6828
0.6876	2.965918	58.6678

Mean, 58.6878

## SECOND SERIES—NICKEL.

Wt. Ni.	Wt. I.	At. Wt. Ni.
0.5120	2.205627	58.7436
0.5200	2.204107	58.7432
0.5246	2.259925	58.7432

Mean, 58.7433

<sup>1</sup> *Ztschr. anorg. Chem.*, 8, 1.

Mean of all, Ni = 58.7155.

For O = 16, these become

Co = 59.517

Ni = 58.863.

*Palladium*.—In 1889 Keiser published his determinations of the atomic weight of palladium, for which, since then, other investigators have found somewhat different values. He has now, jointly with Mary B. Breed, given a new set of determinations, which confirm his former series.<sup>1</sup> As before, palladium-ammonium chloride was reduced in hydrogen, the salt being prepared by two methods and carefully examined as to purity. Two series of experiments are given, with the following weights of material :

#### FIRST SERIES.

$\text{Pd}(\text{NH}_4\text{Cl})_2$ .	Pd.	At. Wt. Pd.
1.60842	0.80997	106.271
2.08295	1.04920	106.325
2.02440	1.01975	106.334
2.54810	1.28360	106.342
1.75505	0.88410	106.341

From sum of weights, 106.325

Reduced to vacuum, 106.246

#### SECOND SERIES.

$\text{Pd}(\text{NH}_4\text{Cl})_2$ .	Pd.	At. Wt. Pd.
1.50275	0.75685	106.297
1.23672	0.62286	106.296
1.34470	0.67739	106.343
1.49059	0.75095	106.353

From sum of weights, 106.322

Reduced to vacuum, 106.245

The atomic weight was computed with H = 1, N = 14.01, and Cl = 35.37. If O = 16 this becomes Pd = 106.51. This is only 0.02 less than the value obtained in the earlier investigation.

*Tungsten*.—A new determination of the atomic weight of tungsten, by Pennington and Smith,<sup>2</sup> leads to a much higher value than that commonly accepted. The older work seems very probably to have been done upon material contaminated

<sup>1</sup> *Am. Chem. J.*, 16, 20.

<sup>2</sup> Read before the Amer. Philos. Soc., Nov. 2, 1894.

with molybdenum, an impurity which was eliminated in this investigation by Debray's method,—that is, by volatilization by means of gaseous hydrochloric acid. The metal, carefully purified, was oxidized in porcelain crucibles, with all necessary precautions, and the following data are given:

Wt. W.	Wt. O <sub>2</sub> .	At. Wt. W.
0.862871	0.223952	184.942
0.650700	0.168900	184.923
0.597654	0.155143	184.909
0.666820	0.173103	184.902
0.428228	0.111168	184.900
0.671920	0.174406	184.925
0.590220	0.153193	184.933
0.568654	0.147588	184.943
1.080973	0.280600	184.913

Mean, 184.921

All weights are reduced to a vacuum, and O = 16 is taken as the standard of reference.

Another paper, by Smith and Desi, was read at the same meeting with that just cited. In this research, the tungstic oxide was purified in the same way, and reduced by heating in a stream of pure hydrogen. The water formed was weighed, and all weights reduced to a vacuum. Computed with O = 16 and H = 1.008, the results are as follows:

Wt. WO <sub>3</sub> .	Wt. H <sub>2</sub> O.	At. Wt. W.
0.983024	0.22834	184.683
0.998424	0.23189	184.709
1.008074	0.23409	184.749
0.911974	0.21184	184.678
0.997974	0.23179	184.704
1.007024	0.23389	184.706

Mean, 184.704

Why this result should be lower than that previously found by Pennington and Smith remains to be explained.

*Thallium*.—Two determinations of atomic weight were made by Wells and Penfield to ascertain the constancy of the element as such.<sup>1</sup> The nitrate was fractionally crystallized until about one-twentieth remained in the mother-liquor, while another

<sup>1</sup> *Am. J. Sci.*, [3], 47, 466.

twentieth had been subjected to repeated recrystallization. Both fractions were converted into thallium chloride, which was dried at  $100^{\circ}$ , and in both the chlorine was estimated by weighing as silver chloride on a Gooch filter. The results were as follows :

	TlCl.	AgCl.	At. Wt. Tl.
Crystals.....	3.9146	2.3393	204.47
Mother-liquor.....	3.3415	1.9968	204.47

Calculated with  $\text{Ag} = 107.92$  and  $\text{Cl} = 35.45$ .

In the report for 1893 Lepierre's work on thallium was given, and the last value cited was  $\text{Tl} = 203.00$ , varying widely from the rest of the series, and affecting the mean. The mean stated by Lepierre was 203.62, and as found by me was 203.57. Lepierre<sup>1</sup> now calls attention to the fact that his value 203.00 was a misprint for 203.60, and that his mean was therefore correctly given. He also gives additional details relative to his work.

*Bismuth.*—The long-standing controversy between Schneider and Classen over the atomic weight of bismuth, has led to a new set of determinations on the part of Schneider.<sup>2</sup> The old method was still used ; namely, of converting the metal into the trioxide by means of nitric acid and subsequent ignition of the nitrate ; but the metal itself was carefully purified. Results as follows :

Wt. Bi.	Wt. $\text{Bi}_2\text{O}_3$ .	Per cent. Bi in $\text{Bi}_2\text{O}_3$ .
5.0092	5.5868	89.661
3.6770	4.1016	89.648
7.2493	8.0854	89.659
9.2479	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660

Mean, 89.657

If  $\text{O} = 16$ , Bi ranges from 207.94 to 208.15, or in mean 208.05, confirming the earlier determinations.

*Tin.*—Incidentally to his paper on the white tin sulphide Schmidt gives one determination of the atomic weight of the metal.<sup>3</sup>

0.5243 gram Sn gave 0.6659  $\text{SnO}_2$ . Hence  $\text{Sn} = 118.48$ .

<sup>1</sup> *Bull. Soc. Chim.*, [3], 11, 423.

<sup>2</sup> *J. prakt. Chem.*, [2], 50, 461.

<sup>3</sup> *Ber d. chem. Ges.*, 27, 2713.

*Anomalous Nitrogen.*—An important discovery has been made by Lord Rayleigh, who finds that nitrogen obtained by purely chemical methods is perceptibly lighter than that from atmospheric air.<sup>1</sup> Equal volumes of the gas, variously prepared, weighed as follows:

By passing NO over hot iron.....	2.30008
" " N <sub>2</sub> O " " " .....	2.29904
" " AmNO <sub>3</sub> " " " .....	2.29869

For nitrogen from air he found:

From air passed over hot iron.....	2.31003
" " " through moist FeO <sub>3</sub> H <sub>2</sub> .....	2.31020
" " " over hot copper .....	2.31026

Investigating the cause of this anomaly, with the co-operation of Ramsay, Rayleigh came to the astonishing results communicated a few months later to the British Association. It was found, in short, that atmospheric air contains a gas heavier than nitrogen, and hitherto unknown. Its density, in a sample as pure as could be obtained, was 19.09, and it was characterized by extraordinary inertness. Whether it is a new element, or allotropic nitrogen, N<sub>2</sub>, remains to be determined. The work is cited here because it shows that the density of nitrogen as hitherto determined, can give no trustworthy value for the atomic weight of the element.

*Miscellaneous Notes.*—Some data bearing upon the atomic weight of tellurium are given by Gooch and Howland.<sup>2</sup> As the homogeneity of tellurium is still uncertain, I omit their details.

Wanklyn's attempt to show that the atomic weight of carbon is not 12, but 6, was noted last year. He has since published more on the subject in a paper on Russian Kerosene,<sup>3</sup> and the matter was also discussed at the Oxford meeting of the British Association.<sup>4</sup>

In a communication upon the Stasian determinations,<sup>5</sup> Hinrichs discusses the availability of silver as a secondary standard in the scale of atomic weights. He makes silver, chlorine, bromine, iodine, and sulphur all Proutian in value. Hinrichs also

<sup>1</sup> *Chem. News*, 69, 231, May 18, 1894.

<sup>2</sup> *Am. J. Sci.*, [3], 48, 375.

<sup>3</sup> *Phil. Mag.*, [5], 37, 495.

<sup>4</sup> *Chem. News*, 70, 87, Aug. 24, 1894.

<sup>5</sup> *Compt. rend.*, 118, 528.

has published his views upon atomic weights *in extenso* in book form.<sup>1</sup>

In conclusion I submit a table of atomic weights revised to January 1, 1894. O = 16 is still retained as the base of the system; but I hope that in another year it will be practicable to return to H = 1.

Name.	Atomic Weight.	Name.	Atomic Weight.
Aluminum.....	27.	Neodymium.....	140.5
Antimony .....	120.	Nickel .....	58.7
Arsenic .....	75.	Nitrogen .....	14.03
Barium .....	137.43	Osmium.....	190.8
Bismuth .....	208.	Oxygen .....	16.
Boron .....	11.	Palladium .....	106.5
Bromine .....	79.95	Phosphorus .....	31.
Cadmium.....	112.	Platinum.....	195.
Caesium .....	132.9	Potassium.....	39.11
Calcium .....	40.	Praseodymium .....	143.5
Carbon .....	12.	Rhodium .....	103.
Cerium .....	140.2	Rubidium .....	85.5
Chlorine.....	35.45	Ruthenium.....	101.6
Chromium.....	52.1	Samarium .....	150.
Cobalt .....	59.5	Scandium .....	44.
Columbium .....	94.	Selenium.....	79.
Copper .....	63.6	Silicon .....	28.4
Erbium .....	166.3	Silver .....	107.92
Fluorine.....	19.	Sodium .....	23.05
Gadolinium .....	156.1	Strontium.....	87.66
Gallium .....	69.	Sulphur .....	32.06
Germanium .....	72.3	Tantalum .....	182.6
Glucinum .....	9.	Tellurium .....	125.
Gold .....	197.3	Terbium .....	160.
Hydrogen .....	1.008	Thallium.....	204.18
Indium .....	113.7	Thorium .....	232.6
Iodine .....	126.85	Thulium .....	170.7
Iridium.....	193.1	Tin.....	119.
Iron .....	56.	Titanium .....	48.
Lanthanum.....	138.2	Tungsten.....	184.9
Lead.....	206.95	Uranium .....	239.6
Lithium .....	7.02	Vanadium .....	51.4
Magnesium.....	24.3	Ytterbium.....	173.
Manganese .....	55.	Yttrium .....	89.1
Mercury .....	200.	Zinc.....	65.3
Molybdenum .....	96.	Zirconium.....	90.6

<sup>1</sup> The True Atomic Weight of the Chemical Elements, and the Unity of Matter. By Gustavus Detlef Hinrichs, St. Louis, 1894.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT  
OF AGRICULTURE, SENT BY H. W. WILEY, No. 13.]

## COLORING MATTER IN THE CALIFORNIA RED WINES.<sup>1</sup>

By W. D. BIGELOW.

Received January 2, 1895.

**D**URING the last three quarters of a century the coloring matter of red wines has been carefully investigated. Those undertaking the work have endeavored to find some reaction or series of reactions, by which the natural coloring matter of the grape could be distinguished from that of other fruit and vegetables with which wines are so frequently adulterated. The introduction of the aniline colors into this industry attracted for a time a portion of the attention which had previously been given entirely to the vegetable colors, and methods have been brought forward by which the former can be recognized. On account of the comparative ease and certainty with which the aniline colors can be detected, wine makers still give their preference to the vegetable pigments, and a method for their detection is still regarded as desirable. A large number of methods have been suggested for this purpose, but most of them have proved worthless, and none of them at all satisfactory.

Among the difficulties which have been encountered by workers in this field, and which have not yet been overcome, are the following:

1. Many of the substances employed for coloring wines are so nearly identical with the natural coloring matter of the grape that it would not be an easy matter to distinguish between them even in freshly prepared solutions.
2. The coloring matter of wine changes materially with age, and different reactions are given by samples of the same variety and from the same locality, but of different vintages.
3. Different reactions are commonly obtained with wines of the same age, but of different varieties or from different parts of the country.

<sup>1</sup> Read before the Washington Section in abstract, November 8, 1894, and before the American Chemical Society, December 27, 1894.

As an example of the difficulties which are met with in making use of any of the methods that have been brought forward, let us notice the action of lead subacetate. According to Vögel this reagent gives a grayish green precipitate with pure wines, while with wines colored with elderberries, the juice of beets, &c., a precipitate colored indigo-blue, red, or some equally characteristic color is obtained. A more careful examination of the method revealed the fact that a number of fortified wines known to be free from foreign coloring matter gave distinct red and violet precipitates, while elderberries and mallow added to some of the lighter wines could not be detected. The same difficulties are experienced to a greater or less extent in all methods which have been suggested, and it is now customary in examining a wine for foreign vegetable coloring matter, to compare it with a wine of known purity, of the same variety, the same vintage, and from the same locality, as the sample under examination.

This work with California wines was done under the direction of Dr. H. W. Wiley, and was in connection with the examination made during the past year of the samples furnished by the California Viticultural Association. In all, ninety-four samples of California red wines were examined. Their age varied from one to seven years.

No wines were available which were known to be colored with vegetable pigments, and the facilities for coloring them were lacking, since wines colored after fermentation are quite different from those fermented after the addition of colored vegetable material to the must. This work was not undertaken, therefore, with the hope of developing a method for the detection of foreign coloring matter in wine, but merely for the purpose of studying the coloring matter of California wines, and of recording the reactions given by some of the reagents, whose reactions with the European wines have been the subject of so much careful study. The number of reagents employed was limited by the size of the samples.

For convenience the methods which were employed are divided into three classes. The methods given in the first class give a red, blue, or violet color with wines containing foreign

coloring matter, and usually a green or grayish green tint when the wines are pure.

The second class of reagents includes certain metallic oxides, such as manganese dioxide and lead dioxide. These have been used in different proportions, sometimes to distinguish between natural wines and those colored with foreign vegetable colors, sometimes between the vegetable colors and coal-tar colors in wine. They have not been found entirely satisfactory, since the amount necessary to decolorize some pure wines is sufficient to destroy even the aniline colors in some that had been artificially colored. Yet they have been found of great assistance in the examination of such wines as claret and burgundy. These reagents were found to destroy almost all the color in California wines when used in the proportions recommended for French claret and similar wines.

The third class includes methods which use chalk treated with albumen and charged with various reagents.

#### CLASS I.

*Lead Acetate—Neutral and Basic.*—The reactions obtained with neutral and basic lead acetate were almost identical. The precipitates were yellowish green, grayish green, gray or brown. No blue, red, or violet colors were obtained.

*Sodium Carbonate.*—In the use of this reagent the solution recommended by Gautier (*Sophistication et analyse des vins*, 4me. edition, page 211) was employed. One cc. of wine was mixed with five cc. of a five-tenths per cent. solution of sodium carbonate. The colors obtained were brown, yellowish brown, and yellowish to grayish green.

*Sodium Bicarbonate.*—Gautier's solution was also employed with this reagent. Eight grams of sodium bicarbonate were dissolved in 100 cc. of water and the solution saturated with carbon dioxide. Equal volumes of this solution and the wine under examination were mixed and the color noted. The reactions obtained were gray or grayish green, with sometimes a tinge of brown.

*Ammonia.*—The action of dilute ammonia on red wine was first pointed out by Chevallier in 1827, and since then it has been commonly used in their examination. The solution used in this

work contained one part of strong ammonia to nine parts of water. This was then added to wine in equal volumes, and the resulting mixture was filtered when turbid. The filtrates were colored various shades of brown and green with an occasional orange-red.

*Ammonium Hydroxide and Ammonium Sulphhydroxide.*—A mixture of twenty cc. of ammonium hydroxide and eight cc. of ammonium sulphhydroxide were diluted with water to one liter, and a portion of five cc. treated with an equal volume of wine. The resulting solutions were brown to yellowish brown.

*Alum and Potassium Carbonate.*—Five cc. of a saturated solution of ammonia alum were mixed with ten cc. of wine, five cc. of a one-tenth solution of potassium carbonate added, and the whole stirred and filtered. The precipitates were gray or yellowish brown with sometimes a tinge of green. The filtrates were sometimes of a light wine color, but were not lilac or wine-colored in any case.

*Alum and Lead Acetate.*—This method is the same as the preceding except that a one-tenth solution of lead acetate is used instead of potassium carbonate. The precipitates were colored yellowish gray to brown except in three cases, when they were of a light wine color.

*Borax.*—Two volumes of a saturated solution of borax were mixed with one of wine. A brown to yellowish brown color was obtained with all wines except one sample of Gutedel, which gave an orange-red color.

*Copper Sulphate.*—Ten cc. of wine were diluted with water to 100 cc. and thirty cc. of a saturated solution of copper sulphate added. The color of the solution was changed in every case to a light olive-green.

*Tartar Emetic.*—Two to three volumes of wine were mixed with one volume of a saturated solution of tartar emetic. The color was changed in every case to a bright cherry-red.

#### CLASS 2.

*Manganese Dioxide.*—100 cc. of wine were shaken for fifteen minutes with fifteen grams of manganese dioxide, and the mixture filtered. The filtrates were light colored, but were not entirely decolorized in any case. Shaking the filtrates with

another portion of fifteen grams of maganese dioxide rendered them almost colorless.

*Lead Peroxide.*—Five grams of lead peroxide were added to twenty cc. of wine, and the mixture well shaken and filtered. Some of the filtrates were entirely decolorized, though in many of them a very light wine color remained.

*Mercuric Oxide.*—Ten cc. of wine were shaken for one minute with three-tenths to four-tenths gram precipitated mercuric oxide (Cazeneuve uses one to one and one-half grams) and filtered. The filtrates were all colorless or light yellow.

#### CLASS 3.

*Sodium Peroxide.*—M. Ruisand uses sodium peroxide to detect aniline coloring matters in wine. He adds ten to fifteen cc. of sodium peroxide to five cc. of wine, allows it to stand twenty minutes, and renders slightly acid with acetic acid. According to Ruisand, both vegetable colors and aniline derivatives are decolorized by the peroxide, while the coal-tar colors are restored by acetic acid.

With the California wines the color is not entirely destroyed, even with twice the quantity of peroxide recommended by Ruisand, and in many cases a marked wine color remained both before and after acidification.

A lump of chalk was cut into pieces about fifteen mm. square and half as thick, and one side of each piece was carefully smoothed with a knife. These pieces of chalk were then immersed for two hours in a ten per cent. solution of egg albumen and dried at 45°. They were then divided into five portions, one of which was reserved for testing the wine without further treatment, and each of the other four immersed for forty minutes in a one per cent. solution of one of the following reagents: Tartar emetic, lead acetate, copper acetate, and zinc acetate. After being dried at 50°, they are ready for use. Three drops of each wine examined were placed on the smooth surface of one block from each of the five divisions given above, the blocks dried at 100° for one hour, and the color noted. Another block from each division was treated with the same amount of wine, dried for twenty-four hours at the temperature of the laboratory, and the color compared with that of the blocks dried at 100°. The colors

obtained were brown, grayish brown, and slate colored. No tinge of violet, blue, or green, was obtained in any case. In every case the color of the block dried at  $100^{\circ}$  was almost, if not exactly, identical with that of the block treated with the same wine and dried at the temperature of the laboratory.

According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. The reactions are not always the same as those obtained with the more ordinary European wines; for instance, a gray, or yellowish, or orange-gray precipitate or solution is sometimes obtained with reagents which are said to give green or grayish green with French wines. On the other hand no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments.

### THE PENETRATION MACHINE—AN EXPLANATION.

BY H. C. BOWEN.

Received January 24, 1895.

ON page 59, January number, 1895, of this JOURNAL, a somewhat vague reference is made to a testing instrument. The identity of the instrument referred to is made manifest to me by the context. The instrument is known by those who have to do with it as the Penetration Machine; first described in print by myself in the School of Mines Quarterly, 10, 297, under the title "An Apparatus for Determining the Relative Degree of Cohesion of a Semi-Liquid Body." The reference above noted, by some mischance, does the instrument and its work injustice. The origin of the instrument was due to pressing needs in the technology of asphalt cements used for paving purposes. These cements, made by different parties using different tempering agents, were very varied, and at the time of the origin of this instrument there was no way other than chewing the cement for foremen to test whether the cement was of required consistency or not. Since that time (1889) thousands of tons of cement have been manufactured, and the whole of this cement has been strictly tested by this machine with nicety and satisfaction. These cements are made in all parts of the country, to a certain penetration number, previously determined as necessary according to the different uses of the cement.

Without this control cements would be used that were not suited for the purpose designed, and much damage would be occasioned in different cities, which damage would much cripple the asphalt paving industry. Cargoes of cement are shipped, one requirement of the cement being that it shall have a certain penetration number previously determined by the contracting parties. Since the introduction of this testing apparatus many qualities of cement have been studied and others discovered. By it we have learned the influence of mild or sudden and marked changes of temperatures, and the consequence of severe cold. It enables us to learn the influence of hardening and softening agents, a matter of great importance in the practical uses of asphalt cement. Thus it is manifest that this instrument has an important and serious part to perform in a great industry, and that its use is far from being an idle pastime.

SCHOOL OF MINES, COLUMBIA COLLEGE,  
N. Y. CITY, January 23, 1895.

### NOTES.

*Argon: A New Constituent of the Atmosphere.*—At the meeting of the Royal Society, held on January 31, the long-expected paper by Lord Rayleigh and Professor Ramsay was read, and a full report has just been received by way of *The Chemical News*, of February 1, from which the following condensed summary is taken: A careful comparison of the nitrogen from urea, ammonium nitrite, and from nitrous and nitric oxid—"chemical nitrogen" with atmospheric nitrogen was made, and gave a weight per liter for

Chemical nitrogen of.....	1.2505 grams
Atmospheric " .....	1.2572 "

Nitrogen which had been extracted from the air by means of magnesium was separated also and gave a figure differing inappreciably from that recorded above for "chemical nitrogen."<sup>1</sup> The nitrogen contained in magnesium nitride was also converted into ammonium chloride and this was found to contain exactly the proportion of chlorine contained in ordinary ammonium chloride. From this it was concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen. After having endeavored in every way possible to detect in "atmospheric nitrogen" known gases to account for the difference in specific gravity the authors finally repeated Cavendish's experiment. It will be remembered that Cavendish found that when air to which oxygen was added, the electric spark passed for several days and the nitrous and nitric acids

<sup>1</sup> See also page 211 of this issue.

removed by soap-lees and finally the oxygen removed by liver of sulphur that "only a small bubble of air remained unabsorbed which certainly was not more than the  $\frac{1}{120}$  of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and can not be reduced to nitrous acid, we may safely conclude that it is not more than  $\frac{1}{120}$  part of the whole." Improving the apparatus of Cavendish so as to shorten the duration of the experiment Rayleigh and Ramsay found that fifty cc. of air left 0.32 cc. of gas. On adding this residue to a fresh fifty cc. of air and repeating the operation the residue now amounted to 0.76 cc.

By passing nitrogen over magnesium turnings contained in a heated tube, 1,500 cc. unabsorbed gas was obtained and after passing this for several days over soda-lime, phosphoric anhydride, magnesium at a red heat, and copper oxide, the gas was reduced to 200 cc. and its density found to be 16.1. After further absorption the density was increased to 19.09. On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen the density of the remaining gas was calculated to be 20.0.

By means of atmolysis using long clay pipe-stems the amount of argon was increased in the air, which finally passed from the pipes so that the nitrogen in it weighed in a total weight of approximately two and three-tenths grams a mean of 0.00187 gram over that of the same volume of "atmospheric nitrogen." By increasing the efficiency of the apparatus the excess was in mean 0.0035 gram.

Experiments then made to prove the absence or presence of argon in chemical nitrogen showed that three liters of chemical nitrogen from ammonium nitrite left three and three-tenths cc. of argon, a part of which is accounted for by an accident. In a second experiment 5,660 cc. of the same nitrogen left three and five-tenths cc. argon. The source of this was found in the water used for confining the gases which absorbs argon from the air in considerable amount, and again gives it up to the confined gases. The amount of argon obtained from the chemical nitrogen was less than  $\frac{1}{10}$  of the normal amount from atmospheric nitrogen. The following quotations from the paper of Rayleigh and Ramsay and from those of Crookes and Olszewski, which followed it, are scarcely susceptible of condensation:

#### *Separation of Argon on a Large Scale.*

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion tube packed tightly with magnesium turnings, and heated



to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing three or four liters. A single tube of magnesium will absorb from seven to eight liters of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 to 150 liters of atmospheric nitrogen, which may amount to four or five liters, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 cc. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost. Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.<sup>1</sup> The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is three liters per hour, about 3,000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7,925 cc., and of oxygen (prepared from potassium

<sup>1</sup> *Chemical News*, 65, 301, 1892.

chlorate), 9137 cc. On the eighth and ninth days oxygen alone was added, of which about 500 cc. was consumed, while there remained about 700 cc. in the flask. Hence the proportion in which the air and oxygen combined was as 79:96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in color.

The final treatment of the residual 700 cc. of gas was on the model of the small scale operations, already described. Oxygen or hydrogen could be supplied, at pleasure, from an electrolytic apparatus, but in no way could the volume be reduced below sixty-five cc. This residue refused oxidation and showed no trace of the yellow line of nitrogen, even under favorable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hour's sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about one and one-half per cent. was clearly, and about three per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

*Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidized except nitrogen. Thus, if

$D$  = density of chemical nitrogen,

$D'$  = " " atmospheric nitrogen,

$d$  = " " argon,

$a$  = proportional volume of argon in atmospheric nitrogen,

the law of mixtures give—

$$ad + (1-a)D = D',$$

or—

$$d = D + (D' - D)/a.$$

In this formula  $D' - D$  and  $a$  are both small, but they are known with fair accuracy, From the data already given—

$$a = \frac{65}{0.79 \times 7925}$$

whence if (on an arbitrary scale of reckoning)  $D = 2.2990$ ,  $D' = 2.3102$ , we find  $d = 3.378$ . Thus if  $N_2$  be 14, or  $O_2$  be 16, the density of argon is 20.6.

A direct determination by weighing is desirable, but hitherto it has not

been feasible to collect by this means sufficient to fill the large globe employed for other gases. A *mixture* of about 400cc. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen, *viz.*, 2.6270. Thus, if  $a$  be the ratio of the volume of argon to the whole volume, the number for argon will be—

$$2.6270 + 0.1045/a.$$

The value of  $a$ , being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave  $a = 0.1845$ ; whence for the weight of the gas we get 3.193, so that, if  $O_2 = 16$ , the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.

#### *Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19.09; and, after sparking with oxygen, it was calculated to be 20.0. The most reliable results of a number of determinations give it as 19.90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19.90 showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was 20.38. But there is some reason here to distrust the weighing of the vacuum globe.

#### *Spectrum of Argon.*

The spectrum of argon, seen in a vacuum tube of about three mm. pressure consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696.56 and 705.64,  $10^{-6}$  mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue or blue violet line of wave-length 470.2; and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most charac-

teristic lines are perhaps those in the neighborhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapor. The approximate wave-lengths are—

487.91.....	Strong.
[486.07] .....	F.
484.71.....	Not quite so strong.
480.52.....	Strong.
476.50.....	} Fairly strong characteristic triplet.
473.53.....	
472.56.....	

It is necessary to anticipate Mr. Crookes' communication, and to state that when the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,<sup>1</sup> who has noticed a similar phenomenon, attributes it to the presence of two gases. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic soda solution.

Prof. Schuster has also found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

#### *Solubility of Argon in Water.*

Determinations of the solubility in water of argon prepared by sparking, gave 3.94 volumes per 100 of water at 12°. The solubility of gas pre-

<sup>1</sup> *Proc. Phys. Soc.*, 1893, p. 147.

pared by means of magnesium was found to be 4.05 volumes per 100 at 13.9°. The gas is therefore about two and one-half times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded \* \* were 2.3221 and 2.3227, showing an excess of twenty-four mgms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is eleven mgms. we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbon dioxide, whose weight was only about midway between that of true and atmospheric nitrogen.

#### *Behavior at Low Temperatures.<sup>1</sup>*

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of -90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical-point and a lower boiling-point than oxygen, and that he has succeeded in solidifying argon to white crystals. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum tube.

#### *Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation—

$$\pi\lambda = v = \sqrt{\left\{ \frac{e}{d}(1 + at) \frac{C_p}{C_v} \right\}},$$

when  $\pi$  is the frequency,  $\lambda$  the wave-length of sound,  $v$  its velocity,  $e$  the isothermal elasticity,  $d$  the density,  $(1 + at)$  the temperature correction,  $C_p$  the specific heat at constant pressure, and  $C_v$  that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound,

<sup>1</sup> The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion—

$$\lambda^2 d : \lambda'^2 d' :: 1.41 : x,$$

where, for example,  $\lambda$  and  $d$  refer to air, of which the ratio is 1.41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about two mm. diameter, and one in one of eight mm., made with entirely different samples of gas, gave, the first, 1.65 as the ratio, and, the second, 1.61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1.276, instead of 1.288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73.6, instead of 74.5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1.39, instead of 1.402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, *viz.*, 1.66 proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.<sup>1</sup>

#### *Attempts to Induce Chemical Combination.*

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat; nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic luster remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum-black does not absorb it, nor does platinum sponge, and wet oxidizing and chlorinating agents, such as nitrohydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action; hence it appears to resist attack by nascent silicon and by nascent boron.

#### *General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mix-

<sup>1</sup> Kundt and Warburg, *Pogg. Ann.*, 135, 337 and 527.

ture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density twenty compared with hydrogen, "atmospheric" nitrogen should contain of it approximately one per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

*Second.*—This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

*Third.*—As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

*Fourth.*—It is in the highest degree improbable that two processes, so different from each other, should manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence, argon can not have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if  $K$  be the energy of translatory motion of the molecules of a gas, and  $H$  their whole kinetic energy, then—

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v}$$

$C_p$  and  $C_v$  denoting as usual the specific heat at constant pressure and at

constant volume respectively. Hence if, as for mercury vapor and for argon, the ratio of specific heats  $C_p : C_v$  be  $1\frac{1}{2}$ , it follows that  $K = H$ , or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury, the absence of interatomic energy is regarded as proof of the monatomic character of the vapor, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself, and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence, it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately twenty, hence, its molecular weight must be forty. But its molecule is identical with its atom; hence, its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be forty.

There is evidence both for and against the hypothesis that argon is a mixture; for, owing to Mr Crooke's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because, on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling that in our future experimental work we shall endeavor to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have, therefore, to discuss the relations to other elements of an element of atomic weight forty. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between nineteen, that of fluorine, and twenty-three, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near forty are—

Chlorine .....	35.5
Potassium.....	39.1
Calcium.....	40.0
Scandium .....	44.0

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium,



and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which can not be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming thirty-seven (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and forty the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, eighty, and rubidium, 85.5; *viz.*, eighty-two, the mixture should consist of 93.3 per cent. of the lighter, and six and seven-tenths per cent. of the heavier element. But it appears improbable that such a high percentage as six and seven-tenths of heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains—



might be expected to end with an element of monatomic molecules of no valency, *i. e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be, perhaps, excused, if they, in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kallas, and Matthews, who have materially assisted us in the prosecution of this research.

Mr. Crookes (before reading his paper) said: Allow me, Mr. President, to take this opportunity of striking the key-note of the chorus of applause

and congratulations which will follow from all chemists present on this most valuable and important paper. The difficulties in a research of this kind are peculiar. Here we have a new chemical element, the principal properties of which seem to be the negation of all chemical properties. Chemists will understand how difficult it is to deal with anything which forms no compounds and unites with nothing. The discovery commenced by a prediction, followed after an interval by realization. Discoveries of this kind are more important and take a higher rank, than discoveries which, more or less, come in a haphazard sort of way. The prediction and discovery of argon are only equalled by the few discoveries of elements which have been made in chemistry by the careful study of the periodic law, and to surpass it we must go back to the predicted existence and subsequent discovery of an unknown planet by Adams and Leverrier.

*On the Spectra of Argon.* By William Crookes, F. R. S., etc. (Abstract.)

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is three mm. At this point the color of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation,"<sup>1</sup> and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the

<sup>1</sup> *Roy. Soc. Proc.*, 1, 88, June, 1891.

circuit, the color of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. It is not easy to obtain the blue color and spectrum entirely free from the red. The red is easily got by using a large coil<sup>1</sup> actuated with a current of three amperes and six volts. There is then no tendency for it to burn blue.

The blue color may be obtained with the large coil by actuating it with a current of 3.84 amperes and eleven volts, intercalating a jar of fifty square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.<sup>2</sup> In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow eighty lines, making 199 lines in all; of these, twenty-six appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminum terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminum terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 amperes and eleven volts; no jar was interposed. At a pressure of three mm. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a millimeter flashes of blue light made their appearance. At a quarter of a millimeter the color of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

<sup>1</sup> The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks twenty-four inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

<sup>2</sup> Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of fifty-two mm. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time when photographing its spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The color immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscopic lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue color. Assuming that the atmosphere contains one per cent. of argon, the three mm. of nitrogen originally in the tube would contain 0.03 mm. of argon. After the nitrogen had been absorbed by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. It is not improbable, and I understand that independent observations have already led the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body, has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

I have prepared tubes containing other gases as well as nitrogen at different pressures, and have examined their spectra both by eye observation and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close

approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed, will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at wave-length 531.7, the aurora line at 557.1, and the helium line at 587.5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapor yield spectra at all like those of argon, and the apparent coincidences in some of the lines which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two members to the family of elementary bodies.

*The Liquefaction and Solidification of Argon.* By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behavior at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cc. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied, had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19.9 ( $H=1$ ); and he thought that at the outside it might contain one to two per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapor pressure at several other low temperatures, while two other series served to determine its boiling and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As a cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding one mm.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end

of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

*Determination of the Critical Constants of Argon.*

As soon as the temperature of liquid ethylene had been lowered to  $-128.6^{\circ}$ , the argon easily condensed to a colorless liquid under a pressure of thirty-eight atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:

Expt.	Temperature.	Pressure.
1.	$-121.2^{\circ}$	50.6 atmos.
2.	$-121.6^{\circ}$	50.6 "
3.	$-120.5^{\circ}$	50.6 "
4.	$-121.3^{\circ}$	50.6 "
5.	$-121.4^{\circ}$	50.6 "
6.	$-119.8^{\circ}$	50.6 "
7.	$-121.3^{\circ}$	50.6 "

In all seven determinations the critical pressure was found to be 50.6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapor pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature.

This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is  $-121^{\circ}$ , and this may be taken as the critical temperature of argon.

At lower temperatures the following vapor pressures were recorded:

Expt.	Temperature.	Pressure.
8.	$-128.6^{\circ}$	38.0 atmos.
9.	$-129.6^{\circ}$	35.8 "
10.	$-129.4^{\circ}$	35.0 "
11.	$-129.3^{\circ}$	35.8 "
12.	$-129.6^{\circ}$	35.8 "
13.	$-134.4^{\circ}$	29.8 "
14.	$-135.1^{\circ}$	29.0 "
15.	$-136.2^{\circ}$	27.3 "
16.	$-138.3^{\circ}$	25.3 "
17.	$-139.1^{\circ}$	23.7 "

In Experiments Nos. 9, 10, and 17, the quantity of liquefied argon was very small, for it filled the tube only to a height of three to five mm., and in the other experiments the column of liquid argon was twenty mm. high or more.

*Determination of the Boiling and Freezing-Points.*

Two hundred cc. of liquid oxygen, prepared in my large apparatus,<sup>1</sup> was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about seventy cc., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature ( $-182.7^{\circ}\text{C}$ ) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below  $-187^{\circ}$  the liquefaction of argon became manifest. When liquefaction had taken place I carefully equalized the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers  $-186.7^{\circ}$ ,  $-186.8^{\circ}$ ,  $-187.0^{\circ}$ , and  $-187.3^{\circ}$ . The mean is  $-186.9^{\circ}$ , which I consider to be the boiling-point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure was 95.5 cc.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 cc. Hence the density of argon at its boiling-point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given can not lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point ( $-187^{\circ}$ ) is much higher than that of oxygen, which I have found under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to  $-191^{\circ}$  by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers:  $-189.0^{\circ}$ ,  $-190.6^{\circ}$ ,  $-189.6^{\circ}$ , and

<sup>1</sup> *Bulletin International de l'Académie de Cracovie*, June, 1890; also Wiedemann's *Beiblätter*, 15, p. 29.

<sup>2</sup> I have redetermined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is  $1.3^{\circ}$  lower than that which I previously recorded.

—189.4°. The mean of these numbers is —189.6°; and this may be accepted as the melting-point of argon.

In the table below I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the appended table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place; *viz.*, between carbon monoxide and oxygen. Its behavior on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

Name.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing pressure.	Density of gas.	Density of liquid at boiling-point.	Color of liquid.
	Below.	Atmos.			mm.			
Hydrogen (H <sub>2</sub> ).....	—220.0°	20.0	?	?	?	1.0	?	Colorless
Nitrogen (N <sub>2</sub> ).....	—146.0°	35.0	—194.4°	—214.0°	60	14.0	0.885	"
Carbonic oxide (CO)...	—139.5°	35.5	—190.0°	—207.0°	100	14.0	?	"
Argon (A <sub>1</sub> ).....	—121.0°	50.6	—187.0°	—189.6°	?	19.9	Abt. 1.5	"
Oxygen (O <sub>2</sub> ).....	—118.8°	50.8	—182.7°	?	?	16.0	1.124	Bluish.
Nitric oxide (NO).....	—93.5°	71.2	—153.6°	—167.0°	138	15.0	?	Colorless
Methane (CH <sub>4</sub> ).....	—81.8°	54.9	—164.0°	—185.8°	80	8.0	0.415	"

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its unexpectedly simple molecular constitution.

Professor Ramsay exhibited two sealed glass tubes which, he said, contained argon, and handed them round. He said that he had been asked by some of his friends to show them the gas. It was, however, quite invisible.

The President (Lord Kelvin).—It will be a satisfaction, I am sure, to anyone present to have one of these tubes in his hand, and to have really handled a glass vessel containing argon.

Dr. Armstrong (President of the Chemical Society).—I am sure, sir, I can say at once that all present to-day who are able to judge of a communication of this kind, and all others outside, will gladly join in the chorus which Mr. Crookes has proposed should be sung. But I should like, speaking more on behalf of the chemists—and I am sure that Professor Ramsay will come over to me for the time and dissociate himself from his colleague—to say that we feel especially indebted on this occasion to Lord Rayleigh, not only on account of the extraordinarily important information which he has placed at our disposal, but more particularly on account of the example which he has set us. You, sir, very



fully alluded in your address this year to the patient manner in which Lord Rayleigh had tracked this new element to its home. I feel sure that the words which fell from you will meet with the warmest approbation everywhere where such work can be understood. (Applause.) The case contained in the paper is undoubtedly a very strong one. Of course, in the hurry of a meeting like this, it has not been so logically brought forward by the reader of the abstract as it might have been, in order to do it full justice; but yet I think it will be quite clear to all who have listened to him that there is a very strong body of evidence which makes it certain that there is in the atmosphere a constituent which has long been overlooked, and a constituent having most extraordinary properties. The paper is not one which, so far as the experimental facts are concerned, can be criticised here. No doubt it will meet with very considerable criticism throughout the world. People will not be satisfied to take all these statements for granted without checking them, and I have not the least doubt that very soon we shall have abundant confirmations of the correctness of the discovery. But, apart from the facts which are brought forward in this paper, there is a portion which is purely—one almost might say, if I may be allowed the expression on such an occasion—of a wildly speculative character; that is the portion dealing with the probable nature of this new element. Professor Ramsay, in his remarks, in a measure let the cat out of the bag in a way which is not apparent when you read the paper, because it is quite clear that, after all, the authors of this communication are not so entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. I think that they have not sufficiently taken into account, in dealing with this evidence, the extraordinary property that this gas possesses. Nitrogen we know is a very inert form of matter, but we know that the character of nitrogen derived from its study in the atmosphere is of an altogether wrong character. We know perfectly well that, taken as an element and treated as an atom, nitrogen is probably one of the most active forms of matter known to us, and that the great difficulty we have in bringing about its association with fresh elements, when we deal with that gas, arises from its extreme activity—its extreme fondness for its own self. Now, if we can judge anything at all from the properties which we know belong to this new element, it is, I imagine, that it is like nitrogen, but “much more so.” It is quite conceivable that the condition which Professor Ramsay pointed out as being the only alternative to the one which is apparently accepted by the authors of the communication is a conceivable condition. It is quite likely that the two atoms exist so firmly locked in each other's embrace that there is no possibility for them to take notice of anything outside, and that they are perfectly content to roll on together without taking up any of the energy that is put into the molecule. There is a great deal to justify a view of this kind. Of course, it can not be discussed independently of what has been said with regard to the new gas

being a mixture; but it is quite clear that, as the discussion has gone on, the statements made in the paper are not so thoroughly accepted as one would think that they were. Mr. Crookes evidently wavers very much on this point with regard to there being two elements present, and I gather as much from Professor Ramsay's account. If we think that we are dealing with two gases here on the evidence of the spectroscope, there is no reason why we should not come to the same conclusion with regard to nitrogen and hydrogen. Oxygen, I believe, has three or four spectra, so that the spectroscopic evidence, after all, although it may be in a measure remarkable, does not appear to justify such a conclusion. The great difficulty that we have, I take it, in accepting the conclusion that we are dealing with an element having a molecular weight of forty, and an atomic weight of forty, arises from the difficulty of placing an element of that kind, which practically seems to me to have driven the authors to the conclusion that, possibly, they are dealing with a mixture. The difficulty would be got over, of course, if we were dealing with a complex body, and I think that was rather hinted at by Professor Ramsay when he referred to one of Olszewski's numbers. This low value, high as it is in comparison with that of nitrogen obtained from the density of the liquid, is a reason which would induce us to place it higher up in the scale of elements, and give it a lower weight. Of course, these are all matters which must be discussed later on more fully; they are matters which can only be discussed very gradually, as we learn more about this substance. As regards its inactivity, very possibly that may be exaggerated. It is very difficult, in a case like this, to find out what are the best conditions to make use of. We know perfectly well that, if we were not in possession of the electric spark, we could scarcely have discovered that nitrogen might be combined with hydrogen to form ammonia direct. We know that we can only bring about the combination of the two if we are in a position at once to remove the product; and that sort of thing may well obtain in a case like this. We know very well that there are comparatively few substances which can be directly associated with nitrogen. It is quite likely that here we are dealing with an element which has still fewer affinities, but it does not follow by any means yet—nor do the authors assert such to be the case—that we are dealing with an element which is entirely inactive even in the form in which it is presented to us. This is not the occasion to discuss the matter fully, but these are points which certainly deserve consideration, and they are some of the first points which make this element of such importance and interest to us as chemists. In conclusion, I can only heartily congratulate the authors on having given us this communication.

Professor Rücker (President of the Physical Society).—I think it is very important on this occasion that we should remember that this is a discussion meeting of the Royal Society, a meeting held in this way for the first time, and a meeting at which reporters are present in order that the net result of the discussion shall go out at once to the world. It is, there-

fore, I think, extremely important that we should distinguish as clearly as possible between the various points of doubt which still may remain with regard to the new element which has been described to-day, and the one certain fact which comes out indisputably from the facts which have been laid before us; namely, that in spite of the doubt which may have existed on the matter for the last few weeks or months, we have it now beyond all question—and I quote the words of the President of the Chemical Society in saying so—that it is certain that we have here a new constituent of the atmosphere. What the importance of this is has already been mentioned, and I want once more to emphasize the fact that this central feature stands out quite clear, apart from whether we have one or two, and apart altogether from whether the various physical quantities which have been laid before us to-day have been measured with the accuracy which may be obtained in the future. But there is one particular point to which I should like to refer. It seems to me that one of the most interesting results arrived at from the physical point of view is the fact that the gas is monatomic. Some of us have had the opportunity of seeing the paper before it was read to-day, and we are therefore, perhaps, aware of one or two facts which, I think, were not actually mentioned by Professor Ramsay. One of these facts is that the experiments required to determine the ratio of the two specific heats were made twice over, or many times over, for all I know, but made in two different ways. They were made in a narrow tube, and they were made in a wide tube; and further check experiments were carried on in which other gases were compared with the new element. There can be no possibility of doubt as to a result of this sort when the experiments are carried out by two such men as Lord Rayleigh and Professor Ramsay. The matter is one which admits of no mistake when conducted in this way, and it must be accepted as certain that the element has that particular ratio of specific heats. Well, then the question arises, What follows from this? I think that it has not perhaps, been quite sufficiently pointed out that, in order that this ratio may be obtained if we are to use the ordinary mechanical theory of gases, it is necessary that the atom with which we are dealing should be regarded as spherical. Of course, I am well aware that our pictures of spherical and the like are, no doubt, only approximations to the truth; but if we are to conceive this atom as consisting of two which are closely united, the one with the other, we must nevertheless suppose, from that point of view, that they are so united as to form a sphere. That is only one way of putting it, but, nevertheless, it does create a difficulty which, I think, has not been altogether referred to before, I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalization of Mendelejeff, that is, after all, an empirical law which is based, at present, upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great

mechanical generalizations which could not be upset without upsetting the whole of our fundamental notions of science.

The President.—Among those present I am sure those who understand most of the subject will be anxious to speak. I now ask any person present to make remarks, and especially to ask questions.

Professor Roberts-Austen.—I should like to say that, when this beautiful discovery was communicated to the British Association, I ventured to point out that it was not too soon to consider its relation to the great metallurgical industries in which air is largely employed. In the Bessemer process alone you take some ten tons of iron and put it into a vessel called a converter. It is melted, and air is passed through to remove the carbon, silicon, phosphorus, and other impurities. That means that no less than 100,000 cubic feet of air pass through the metal. Therefore, 1,000 cubic feet of argon have gone somewhere. Now, I have taken Bessemer-blown metal, which has been treated with ferro-manganese, and have pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen I have not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. I have taken a small quantity of air and abstracted argon from it, and obtained exactly the proportion that the authors say it contains, so I am perfectly certain that the manipulation is correct. But it remains to be seen whether the argon finds its way into the iron, as nitrogen undoubtedly does, and, if it does, whether it stays there, because there are certain peculiarities that make Bessemer metal different from other kinds of steel, and it would be most interesting if we could succeed in tracing it to some of this 1,000 cubic feet of argon which has either passed into the air or into the iron. I should just like to say that I could have wished that the authors of the paper had dialyzed the air through india-rubber, and not have merely used clay pipes. As one so long associated with Graham, I can only say how delighted he would have been had he known that his method would have been used by the authors of this paper, one of whom occupies Graham's own chair at University College.

Lord Rayleigh.—I have very little to add to the account which my colleague, Professor Ramsay, has given of this research. The research has been, in many respects, a very difficult one. I am not without experience of experimental difficulties, but certainly I have never encountered them in anything like so severe and aggravating a form as in this investigation. Every experiment that one attempts takes about ten days or a fortnight to carry out to any definite conclusion, and the result has been, of necessity, much less progress than we could have hoped for, and many of the questions have been left open which we could have wished to settle. One such question has just been alluded to by Professor Roberts-Austen; namely, the character of the gas transfused through india-rubber. That experiment has been upon our program, I may almost say from the first, but hitherto time has not been found to carry it out. The

difficulties of those parts of the research with which I have been more particularly connected have been very great. The preparation of the gas in sufficient quantity to experiment with at all has been no easy matter, and some of the results, such as those relating to the density of the gas, are consequently not so satisfactory and not so thoroughly elaborated as one could have wished. One point that has been mentioned relates to the argument in favor of the monatomicity of the gas. Of course, what is directly proved by the experiment, if it is good, is that the whole, or nearly the whole, of the energy put into the gas, when it is heated, is devoted to increasing the energy of its translatory motion, and that no margin remains over, as in the case of other gases, to be attributed to intermolecular or interatomic motion. At first sight it seems rather a strange thing that there should be no rotation in the molecules of the gas. How can it be? Can they be without rotation, or can the energy of their rotation be so small as to be negligible in comparison with the energy of the motion as a whole? That is a difficulty which I think has not been thoroughly met hitherto by the cultivators of the dynamical theory of gases; but apparently here we may accept it that no such energy exists, or that no such energy exists in any appreciable degree. Of course, that condition is quite well met by the suggestion which has been put forward, and which has also been communicated to us by Professor Fitzgerald, of Dublin, who writes as follows:

"The reason why the ratio of specific heats of 1.66 is supposed to prove monatomicity in a gas is because in a monatomic gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence, the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves, as a whole, as if it were monatomic."

That argument is, no doubt, perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figdres roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible for such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. That is difficult, and I think the only interpretation is, that the gas is monatomic. No doubt the whole subject is one about which we know exceedingly little, mercury vapor being the only other gas at present which exhibits a similar property. I am not sure that any other point has been raised, but if any questions are asked, Professor Ramsay and myself are quite ready to give further explanations, so far as it is in our power to do so.

The President.—I wish to make a remark, not as from the chair, but with reference to the question which is now before us, as to the condition

under which the ratio of the specific heats could be exactly one and two-thirds. I do not admit that a spherical atom could fulfill that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. Neither can I admit that excessively rigid connection between two atoms could give it the quality of having no capacity whatever for a relative vibratory movement. It would need infinitely stiff connections to give it no capacity for relative vibratory movement; and if it had infinitely stiff relative connection the connection of the two bodies would be indissoluble, and they would remain one. In fact, I think that the only kind of atom that we can conceive as giving, in the dynamical theory of heat, rigorously the ratio of one and two-thirds for the specific heat is the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighboring points with a force depending upon distance. I have now to ask for any further remarks. I do not wish to close this most interesting discussion. I hope we shall have further discussion and further questions.

If there are no more remarks and no questions to be put, I desire now, in the name of the Royal Society, to thank the Senate of the University of London for their hospitality on this occasion, a hospitality which I am sure we have all very much enjoyed. I have great pleasure in joining with the President of the Chemical Society, and the President of the Physical Society in congratulating Lord Rayleigh and Professor Ramsay on the brilliant success already obtained. (Great cheering.) I join with my brother Presidents in wishing them more and more success in the continuation of their work, and in thanking them heartily in the name of the Royal Society for the communication which they have given us this day. (Cheers.)

*Calcium Sulphite Stalactites and Stalagmites.*—Under a number of large wooden tanks, in which "Bisulphite of Lime," of the trade, has been stored for a year or more, a curious stalactitic formation was observed.

The "Bi-sulphite of Lime," seeping through minute openings in the bottoms of the tanks, had been precipitated as calcium sulphite by the evaporation of free sulphurous acid, in a manner perfectly analogous to the natural formation of stalactitic deposits of calcium carbonate.

The stalactites examined were from six to eighteen inches in length, generally with a small hole vertically through the center, granular in structure, more or less stained with iron, and partially oxidized to calcium sulphate. A few were made up of concentric rings of granular crystals, alternate rings being more deeply stained with iron. One specimen, radiately fibrous in

structure, was beautifully crystallized. The stalactites were usually irregular cones with the altitude from five to ten times the diameter of the base.

In many cases the stalactite and stalagmite had become united forming an irregular cylindrical column.

The stalagmites examined were all granular in structure and usually less deeply stained than the corresponding stalactites. One specimen was white and very well crystallized. Like the stalactites they were usually more or less oxidized. The vertical axis was shorter, in proportion to the diameter of the base, and the apex more rounded, than in case of the stalactites.

The phenomenon is deserving of attention as an illustration of the well-known analogy between the sulphites and carbonates of the alkaline earth metals, as regards insolubility in water, but ready solubility in water containing sulphurous or carbon dioxide respectively. It is also interesting as showing a further analogy between two classes of salts which do not fall in the same period in the Mendelejeff classification.

DAVID HANCOCK.

CUMBERLAND, MD., January 18, 1895.

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### NEW BOOKS.

A TEXT-BOOK OF INORGANIC CHEMISTRY. DESCRIPTIVE, THEORETICAL, AND PRACTICAL. A MANUAL FOR ADVANCED STUDENTS. BY ALFRED A. BENNETT, PROFESSOR OF CHEMISTRY IN THE IOWA COLLEGE OF SCIENCE, AGRICULTURE, AND THE MECHANIC ARTS. 2 Vols., 12 mo. 11 Illustrations. New York, Boston, Chicago: Silver, Burdette & Co. 1892 and 1894. Introductory price, \$1.50 per volume.

It has lately been stated in a book review in these pages that there is doubtful room for new text-books on inorganic chemistry; and, in view of the important number of standard works of acknowledged value and usefulness extant, most instructors will heartily concur in this view. Every teacher, however, has his own ideas of how best to present the subject to his students to enable them to readily and intelligently grasp it, and whatever may be the text-book employed, it can in any case be followed only as a general guide and be adapted to the needs and conditions in each case. The work before us may fairly claim to be of such general adaptability as to be useful in most cases, and

particularly in those in which objective teaching, now properly so prevalent, has been adopted. It is essentially a laboratory guide rather than a lecture adjuvant, a manual rather than text-book, and its aim is to furnish such schemes for practical work with chemicals and apparatus in the hands of students as will lead them by actual practice and observation to grasp the fundamental principles of the science, describing the properties of the elements and compounds little further than is necessary to the development of these principles or to emphasize the facts that should be gleaned from observation and experiment.

The first volume (pp. 357) of the work is devoted to the so-called non-metallic elements, and after the usual brief discussion of matter and energy, the relations of physics and chemistry, and the conservation of matter and energy, begins with a study of hydrogen and the halogens and the combinations of the former with the latter. From the properties and reactions covered in this study are developed the hypotheses, theories, and laws which constitute, as it were, the axioms of chemistry. This general principle is followed throughout the work, and the facts concerning each element are studied in the following order: 1. Occurrence and distribution; 2. Methods of preparation; 3. Preparation; 4. Experimental study; 5. Physical properties; 6. Chemical properties; 7. Name, derivation, meaning, and symbol; 8. History; 9. Uses; 10. Special tests for recognition of the elements; 11. (For compounds.) The determination of molecular formulas. And along with this, theoretical considerations are developed in a logical manner.

Under the caption "Experimental Study" are offered directions for making experiments which, it is expected, will be explained to the class in the lecture room and will be carried out later in the laboratory by the students, who will likewise be required to keep copious notes of their operations and observations. Supplemental to these directions are offered certain arithmetical problems illustrative of the principle and properties developed, and unfinished equations which the student is directed to complete.

An interesting and novel feature of the book is the limited study of potassium and sodium in connection with, and imme-



diately following, that of the compounds of hydrogen, the halogens, and oxygen, thus "introduced in order that the learner may have some facts to use in the consideration of acids and bases."

The second volume (pp. 366) is devoted to the metallic elements, their properties, and reactions (pp. 299); the classification of the elements in accordance with the periodic law (pp. 18); a system of qualitative analysis, (pp. 47), concluding with a table of seventy-two elements with their atomic "masses," prepared by F. W. Clarke and a blank table of solubilities of salts to be filled by the student as he determines these properties in his experiments.

"Mass" is used in preference to weight and the system of spelling recommended by the committee of the American Association for the Advancement of Science followed throughout.

Having developed the significance of valence and atomic mass in the first volume, the author devotes considerable space in this volume, in connection with each metal, to the facts which determine its classification with regard to these properties; and in view of the difficulties which students frequently meet in acquiring familiarity with them, this provision will, in many cases, prove most valuable.

The volumes are, each of them, provided with excellently arranged indexes, are of such form and size as to be convenient for use either in the study, the lecture room, or the laboratory, and are offered in attractive style both as to binding and typography.

WM. MCMURTRIE.

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES AS PRACTICED IN GEORGETOWN COLLEGE, D. C. pp. 61. New York: American Book Company. 1894. Price \$1.50.

This small book is divided into four parts: I. Basic Analysis. II. Acid Analysis. III. Preliminary Examination. IV. Solution of Solid Substances.

The bases are grouped and numbered according to Fresenius. The method of describing the properties and characteristic reactions of the elements of each group is somewhat different from that commonly used. A brief note of the properties of the element itself is first given, then the names and formulas of the

most common soluble compounds, and then the insoluble compounds under which head the characteristic reactions are given by first naming the insoluble compound or precipitate and then stating how it is formed, giving its properties, etc. Although the author states that "only these facts have been selected which are indispensable in a course such as the one for which the book is intended," it would seem that too large a number of characteristic reactions are either omitted or reserved to the analytical tables and explanations of the tables, and that in consequence the student hardly did a sufficient number of these important experiments before going on with a group separation.

This form of arrangement, however, may possess some advantages over the usual method of procedure. Certain it is that the explanations connected with each table of analysis is one of the best features of the book and bears evidence of careful and conscientious work on the part of the author. In treating of the acids the usual preliminary experiments upon the characteristic reactions of the individual acids of each group are entirely dispensed with, and instead one passes immediately to their separation and detection. To be sure the special tests applied to the separate portions of the original solution are characteristic. And the explanation of them is apt, still here again it would seem that some experience should be had in noting their deportment toward certain reagents before going to their separation. The preliminary examination and the solution of substances is substantially the same as ordinarily given in most text-books.

W. J. KARSLAKE.

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**ADDENDUM.**—Professor Mabery makes the following addition to his article in the February number, page 105, after the words "Morley determined with the utmost precision the proportions of oxygen without finding any appreciable variations," insert the following:

In certain conditions of the atmosphere, when a vertical descent of the upper portions occurs, Professor Morley observed a deficiency in oxygen equivalent to 0.16 per cent.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE SUPERIORITY OF BARIUM HYDROXIDE SOLUTION AS AN ABSORBENT IN CARBON DETERMINA- TIONS IN STEEL.<sup>1</sup>

By JAMES O. HANDY, Chemist of The Pittsburg Testing Laboratory, L't'd.

Received January 8, 1895.

THE use of barium hydroxide solution as an absorbent for carbon dioxide is not new. It has long been used for that purpose in air analysis. It has also been used to a very limited extent in carbon determinations in steel.

As an absorption apparatus, Geissler potash bulbs are compact and convenient; they can be used several times without refilling, and are therefore very widely employed. Their use is, however, accompanied by at least one disadvantage; *viz.*, the error caused by differences in the temperature or degree of moisture in the laboratory air at the beginning and end of a combustion. This error sometimes amounts to more than do the small quantities of carbon dioxide whose exact weight it is desired to ascertain. This fact is well known and the error is to a considerable extent eliminated by the following precautions:

(a) Take the last weight of the bulbs from one combustion as the initial weight for the next; if the bulbs have been freshly filled with potassium hydroxide, a blank combustion is always made before taking the weight of the bulbs.

(b) During combustions, keep the bulbs in a covered box and thus shield them as completely as possible from moisture, dust, and heat.

<sup>1</sup> Read at the Boston meeting, December 27, 1894.

(c) Weigh them always at the same interval after finishing the combustion.

In the Pittsburgh atmosphere, fog and smoke are often present. The changes in the degree of moisture are frequently very considerable, even in a few hours. Hence carbon determinations by potassium hydroxide bulbs are especially difficult.

When barium hydroxide solution is used as an absorbent for carbon dioxide it is possible to finish the analysis in at least three ways :

(1) The barium carbonate may be filtered off, washed, ignited, and weighed. This has been done successfully by Mr. Alex. G. McKenna, of Pittsburgh. He uses a special absorption apparatus to which the barium carbonate does not adhere.

(2) The excess of barium hydroxide solution may be titrated :

(a) By a standard oxalic acid without filtering off the barium carbonate, or (b) by standard sulphuric acid after filtering off the barium carbonate.

In either case phenolphthalein is the indicator which is used. I have found difficulty when using the oxalic acid titration in getting a satisfactory end point. With the sulphuric titration, no such trouble was experienced.

The facts that the ratios between C and  $\text{Ba}(\text{OH})_2$ ,  $\text{BaCO}_3$ , and  $\text{H}_2\text{SO}_4$ , are so much less than that of C to  $\text{CO}_2$ ,

$$\text{C} : \text{BaCO}_3 = 12 : 197.4 = 1 : 16 +$$

$$\text{C} : \text{Ba}(\text{OH})_2 = 12 : 171.4 = 1 : 14 +$$

$$\text{C} : \text{H}_2\text{SO}_4 = 12 : 98.0 = 1 : 8 +$$

$$\text{C} : \text{CO}_2 = 12 : 44.0 = 1 : 3 +$$

show the great advantage possessed by the barium hydroxide methods over the potassium hydroxide absorption for carbon dioxide.

When we consider also that the use of standard barium hydroxide and a titration method does away with the uncertain atmospheric moisture factor, it is at once plain that the method has several distinct points of superiority over the potassium hydroxide method.

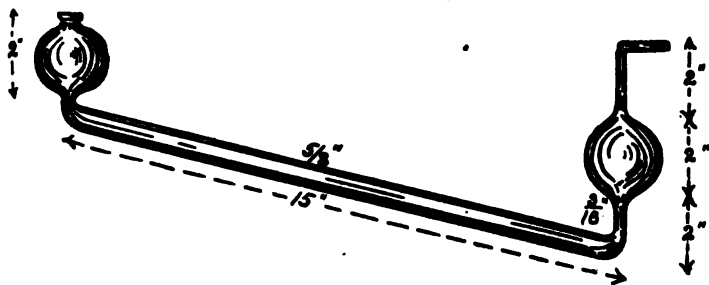
*Method for Steels of 0.06 to 0.20 per cent. carbon.*—Dissolve, by shaking in a glass-stoppered bottle, ten grams or more of 0.06 per cent. carbon steel or five grams of 0.20 per cent. steel in a mixture of copper and potassium chloride solution, one pound in

1,400 cc. of water, and hydrochloric acid. Use 600 cc. of the former and forty cc. of the latter for ten grams of steel and proportionately, more or less, for other amounts. Filter on asbestos which has been ignited in oxygen, wash as usual, and dry the carbon residue at  $100^{\circ}$  C. Transfer to combustion tube and make combustion as usual. Regulate the oxygen current so that one bubble starts up the absorption tube just as its predecessor reaches the top.

Between the combustion tube and the absorption apparatus I place only a U tube containing calcium chloride in the first limb and anhydrous copper sulphate in the other.

The absorption apparatus consists of two glass tubes like the one shown in the sketch.

Each tube contains fifty cc. of barium hydroxide solution. Tubes of this shape seem to give the bubbles of gas a rapid rotating motion as they rise through the barium hydroxide solution. As a result, the absorption is very perfect. This is an important point. Many forms of apparatus fail utterly in this particular.



When the combustion is complete and pure air or oxygen has been passed long enough to expel all carbon dioxide, the absorption apparatus is disconnected and the contents filtered.

During the filtration, air purified by bubbling through potassium hydroxide solution is kept playing on the surface of the barium hydroxide solution. This prevents the formation of barium carbonate by the action of atmospheric carbon dioxide on the excess of barium hydroxide. Since laboratory air is often very impure, this precaution is imperative.

The barium carbonate precipitate is washed with distilled water which is free from carbon dioxide. That which has been freshly distilled is best. The water from wash-bottles or flasks is unavailable. When kept in a stock carboy, connected with the laboratory still, I have always found my distilled water free from carbon dioxide. The excess of barium hydroxide solution is quickly titrated after filtering off the barium carbonate and washing it with water free from carbon dioxide.

Standard sulphuric acid is used, with phenolphthalein as indicator. Certain precautions are necessary when filling the absorption tubes with barium hydroxide solution.

By connecting a potassium hydroxide wash-bottle and calcium chloride tube with the blast-pipe, pure air can be easily obtained.

Force pure air through the absorption tubes for ten minutes; then close them by rubber connections. While drawing up the fifty cc. of barium hydroxide solution have the pure air current passing into the barium hydroxide bottle. When ready, allow the barium hydroxide solution to run into the absorption tube closing the same again and keeping so until ready to connect with the combustion train.

## EXPERIMENTS.

	KOH Method Chemist "L" "C"	Ba(OH) <sub>2</sub> method Chemist "H"	Color test KOH standard.
Steel "A" Carbon	0.14	0.134	0.14
" 11834.7 "	....	0.109	0.11
" 11857.0 "	0.17	0.178	0.17
" "M" "	0.08%	<div> 0.090    0.093  0.091 and 0.092 </div>	0.08

## STANDARD SOLUTIONS.

*Standard Barium Hydroxide Solution.*—Twenty grams of barium hydroxide are dissolved in water in a stoppered graduate and then made up to one liter. Filter into a bottle containing pure air, (air which has passed through the potassium hydroxide wash-bottle). Keep a current of pure air playing on the surface of the solution during filtration. It will then remain clear and bright even if the laboratory air is quite impure. Of this solution fifty cc. are more than sufficient for the carbon from five grams of two-tenths per cent. carbon steel. A second absorption tube is usually kept in the train but is rarely necessary.

*Standard Sulphuric Acid.*—A decinormal solution is used. Of this one cc. = 0.0006 gram carbon.

This method is best adapted for low carbon steels, because only small quantities of barium carbonate have to be filtered and washed.

When analyzing high carbon steels I have used smaller weights of steel (one or two grams) and have rinsed the barium carbonate and excess of barium hydroxide solution into a liter flask; after making up to one liter with pure water, I filter off 200 cc. and titrate by standard sulphuric acid. Steel 11920 gave 1.35 per cent. and 1.35. per cent. carbon by this method.

The work which I have been able to do seems to me to suffice to call attention to the merits of the barium hydroxide methods.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[Continued from page 147.]

The interaction involved the formation of gypsum and aluminum chloride, which, in turn, precipitated the gelatin and converted it into a leatherlike insoluble substance. The object was to fill the pores of the fabric with gypsum and cover the surface with a hard binding material. Sir Frederick Abel, in reporting on the feasibility of this process found that it rendered the canvas very difficult of ignition, but that it also gave to it a degree of rigidity and harshness which forbade its use. In 1856 Maugham<sup>1</sup> patented the use of ammonium phosphate and starch; and in 1857 Thouret<sup>1</sup> patented the use of a mixture of three parts of ammonium chloride and two parts of ammonium phosphate, adopting these proportions on account of cheapness, although the ammonium phosphate alone gave most excellent results.

During this period the importance of better protection for the scenery of theaters was recognized. After a serious fire in the Berlin opera house, the custom was inaugurated of soaking all scenery in a strong alum solution.<sup>2</sup> In 1857 a commission in

<sup>1</sup> Amer. Arch., 13 and 14.

<sup>2</sup> Frémy, *Dict. de Chimie*, 10.

Paris carefully examined the subject, and in accordance with their recommendations the order was issued to have all scenery in theaters impregnated with waterglass.<sup>1</sup> After the lapse of some years it was found that scenery thus treated possessed but slight resistant power. The explanation advanced is that the waterglass, on drying, contracts steadily until the solid particles finally sit very lightly on the yarn of the canvas. Another is that a solvent action is exercised by the water in the water-colors often used by scenic artists. It has been suggested by Hexamer that the impregnation with waterglass could be advantageously followed by treatment with hydrochloric acid, thus precipitating silicic acid directly in the fibers of the yarn, a process practically similar to that of the use of mordants in dyeing.

Versmann and Oppenheim,<sup>2</sup> in 1859, reported to the British Association for the Advancement of Science the results of an elaborate and extended study on the use of salts in treating fabrics, including some forty different substances in the range of their experimentation. Their tests were made on muslin free from starch, weighing 33.4 grams to twelve square inches; and more in the direction of ascertaining the strength of the most effective solution, rather than the weight of a given salt absorbed. After immersion in a solution the excess was removed by pressing and not by wringing. Tests were conducted on a large scale in muslin works and laundries. None of the salts recommended to that time were found available where the operation of ironing was to be performed. Either a smooth surface could not be obtained, or the material was injured on the application of heat.

The valuable results of Versmann and Oppenheim may be briefly summarized as follows:

KCN—very effective in a ten per cent. solution, but poisonous and expensive.

$\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ —both very effective in a ten per cent. solution, but the one is efflorescent and the other deliquescent.

$\text{NaHCO}_3$ —very effective in a six per cent. solution, but carbon dioxide is rapidly lost and the protective power disappears.

<sup>1</sup> Frémy, *Dict. de Chimie*, 10.

<sup>2</sup> Loc. cit.



$\text{Na}_2\text{B}_4\text{O}_7$ —very effective, but on warming, boric acid is liberated and attacks the fabric.

$\text{NaOH}$ —effective in eight per cent. solution.

$\text{Na}_2\text{SO}_4$ —no effect.

$\text{NaHSO}_4$ —twenty per cent. solution is protective, but the stuff is gradually attacked.

$\text{Na}_2\text{SO}_3$ —twenty-five per cent. solution is protective, but the stuff is gradually attacked.

$\text{Na}_2\text{HPO}_4$ —a saturated solution is effective, but the fabric becomes perfectly stiff.

$\text{Na}_2\text{SiO}_3$ —the fabric is strongly attacked and the appearance affected.

$\text{Na}_2\text{SnO}_3$ —protective, but attacks the fabric.

$(\text{NH}_4)_2\text{CO}_3$ —too volatile.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ —renders the fabric combustible.

$(\text{NH}_4)_2\text{B}_4\text{O}_7$ —a five per cent. solution gives good protection, but the acid is easily liberated and corrodes.

$(\text{NH}_4)_2\text{SO}_4$ —a ten per cent. solution is very effective, but the salt is deliquescent.

$\text{NH}_4\text{Cl}$ —a twenty-five per cent. solution gives excellent results, but stiffens the fabric.

$(\text{NH}_4)_2\text{HPO}_4$ —gives excellent results alone or when mixed with ammonium chloride as in Thouret's patent. Maugham's mixture of this salt with starch was not available on account of uneven distribution throughout the mass.

$(\text{NH}_4)_2\text{SO}_4$ —when rendered perfectly neutral by a little ammonium carbonate, this yields the best results of all the ammonium salts. Chevalier's mixture of this salt and borax attacks fabrics at a summer temperature.

$\text{SnCl}_2$ $\text{SnCl}_4$ $\text{SnCl}_2 \cdot 2\text{NH}_4\text{Cl}$	$\left. \begin{array}{l} \\ \\ \end{array} \right\}$	All these are good protectives, but attack the material.
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The following salts give good protection when used in solutions of the strength indicated, but are not available on account of price, or corrosive, or other properties;  $\text{BaCl}_2$ , fifty per cent. solution,  $\text{CaCl}_2$ , ten per cent.,  $\text{Al}_2(\text{SO}_4)_3$ , seventy-seven per cent.,  $\text{KAl}_2(\text{SO}_4)_3$ , thirty-three per cent.,  $\text{NH}_4\text{Al}_2(\text{SO}_4)_3$ , twenty-five per cent.,  $\text{FeSO}_4$ , fifty-three per cent.,  $\text{CuSO}_4$ , eighteen per cent.,  $\text{ZnSO}_4$ , twenty per cent., and  $\text{ZnCl}_2$ , eight per cent.

Unsuccessful attempts were made to fix upon the fibers such protective salts as  $\text{BaSO}_4$ ,  $\text{Al}_3(\text{PO}_4)_3$ , and various silicates. Zinc oxide and aluminum oxide gave good results, but would not adhere when washed. Antimony chloride was effective and withstood water, but not soap or soda. Stannous borate, phosphate, and arsenate gave good protection and withstood washing, but gave a yellow tinge to the fabric. Zinc and calcium stannates, while efficient protectors, would not withstand soap or soda. Stannic oxide was fixed permanently but imparted a yellow color. It seemed to be well adapted for coarse material, sail-cloth, canvas, etc.

For light stuffs, to be ironed, sodium tungstate was found to be the best agent, and the most effective solution is one of 28° Tw. or 1.14 sp. gr., containing also about three per cent. of sodium phosphate in order to prevent the formation and precipitation of the acid tungstate.

Where the hot iron is not to be applied directly, ammonium sulphate can be advantageously employed in a ten per cent. solution. The fabric is to be dried in chambers; the ordinary colors on prints, except madder purple, are unaffected.

Versmann and Oppenheim at first sought to produce, artificially, conditions similar to those existing in animal fibers such as silk and wool, which are not inflammable, and which contain about eighteen per cent. of nitrogen. Experiments to incorporate nitrogenous substances such as glue or albumen into vegetable fiber were without practical result, although it was found possible by the use of urea to introduce into muslin thirteen per cent. of nitrogen, rendering it thereby unflammable.

Essentially the same object is obtained, as we have seen, by the use of ammoniacal salts.

Sir Frederick Abel<sup>1</sup> made reports in 1859 and 1860 to the English Ordnance Department on Versmann and Oppenheim's results, especially with reference to the protection of canvas. The advantages of sodium tungstate for light fabrics were fully confirmed by him. The availability of stannic oxide for sail-cloth was likewise confirmed. Sail-cloth was most effectively deprived of its inflammability thereby, and the protective agent was permanently fixed in the fabric, being affected neither by friction nor

<sup>1</sup> Amer. Arch., 13 and 14.

by repeated washing, while the strength of the canvas was not diminished. The only objections to the use of stannic oxide, were: First, the notable increase in weight amounting to fifty per cent. of the original weight of the canvas; and, second, the comparative costliness. While the first objection was regarded by Abel as practically inseparable from the permanent fireproofing of fabrics, the second he considered much more serious. Accordingly, we find him, shortly after, patenting and submitting to the Ordnance Department, a cheaper process for fireproofing canvas, consisting of the deposition in the fiber of a double sodium and lead silicate. Boiling solutions of basic lead acetate and of waterglass were used. I have not been able to ascertain how extended a use was made of this process. Abel in his reports states that he finds saturation with a solution of waterglass alone an efficient protective; but that its value is temporary only. He sums up the difficulties to be encountered in fireproofing fabrics as follows:

(1) The protective material renders the fabric harsh and rigid; or (2) it absorbs moisture and keeps the fabric damp; or (3) it affects the strength and durability of the fabric; or (4) it is easily detached by rubbing or shaking; or (5) it is soluble in water and must be renewed after wetting.

In 1870 Abel<sup>1</sup> recommended to the Ordnance Department treatment with calcium chloride for rope mantelets on board warships in order to keep them damp and prevent ignition during the firing of guns.

In 1871 the Austrian chemist Patera<sup>2</sup> introduced the use of magnesium borate as a protective for fine fabrics and delicate colors. The materials are soaked in a bath of three parts of borax and two and one-half parts of magnesium sulphate in twenty parts of water with the necessary amount of starch, then wrung between cloths and dried. For coarser stuffs he found mixtures of ammonium sulphate and gypsum effective.

In 1882 a special committee of the Franklin Institute of Philadelphia reporting on safety devices for theaters, gave the results of their experiments on the fireproofing of scenery and gauze.<sup>1</sup> They obtained the best results with the material devised by Dr.

<sup>1</sup> Amer. Arch., 13 and 14.

<sup>2</sup> Flammenschutzmittel, Wien, 1871.

J. Papen, of Frankfort, Germany. The details of its composition are not given, but it has rendered excellent results in the Frankfort opera house, yielding efficient protection, not altering in time, nor affecting the strength or color of the fabrics, and producing no injurious effect on the voices of singers or actors. The committee obtained also very good results from the use of ammonium sulphate, of silica precipitated on the fiber, and from the processes of Gantsch and Judlin, details of which are also lacking.<sup>1</sup>

This question of fireproofing scenery, etc., in theaters had already been the subject of considerable investigation. In 1877 a committee of the House of Commons took evidence on the matter, and we find Mr. Henderson, of the Criterion theater testifying that he used regularly sodium tungstate in the preparation of new scenery; although it was not available for old scenery.

A committee of the London Society of Arts,<sup>1</sup> in 1883, made a report on the same subject, recommending sodium tungstate as the best safeguard for scenery. They found on investigation, that the scenery in nearly all London theaters was treated with some fire-proof preparation; most having as a basis a borate or a silicate. They add in their report: "these compositions do not prevent the evolution of gas when an article is exposed to sufficient heat; and the gas takes fire and burns. When the external source of heat is removed, no more gas is evolved, and combustion ceases. Prepared articles burn when exposed to sufficient heat, but do not support combustion. One effect of this is that it is very much more difficult to set such materials on fire; and this either prevents the breaking out of the fire, or renders it much more easy to deal with when broken out."

The theaters of Paris had already used largely for protecting scenery, a solution of the following composition devised by Martin and Tessier:<sup>2</sup>

Ammonium sulphate.....	8
Ammonium carbonate.....	2
Boric acid.....	3
Borax.....	1
Starch.....	2
Water.....	100

<sup>1</sup> Amer. Arch, 13 and 14.    <sup>2</sup> Frémy, *Dict. de Chimie*, 10.

Among recently introduced preparations for the purpose in view, the efficacy of which has not been fully tested, are the following :

Vendt and Herard,<sup>1</sup> 1885. A solution of eight parts ammonium chloride, ten parts ammonium sulphate, two and one-quarter parts sodium thiosulphate, four and one-half parts borax, and seventy-two parts water.

Winckelman : <sup>2</sup> —Manganese chloride.....	33 parts.
Glacial phosphoric acid...	20 "
Borax.....	10 "
Magnesium chloride.....	12 "
Magnesium sulphate.....	25 "

Fabrics are boiled for six hours in this solution and become thoroughly impregnated with insoluble double salts.

Martin and Tessier : <sup>2</sup> —Boric acid.....	6 parts.
Borax.....	3 "
Ammonium chloride.	15 "
Water .....	100 "

Used chiefly for cordage, sail-cloth, canvas, and straw, the materials being steeped in the solution.

Vogt : <sup>2</sup> —Ammonium chloride.....	2 parts.
Zinc sulphate.....	1 "
Water.....	20 "

Starch as needed.

Subrath : <sup>2</sup> —Alum.....	5 "
Ammonium phosphate.....	5 "
Water .....	90 "

Hattin :<sup>2</sup>—Calcium dihydrogen phosphate, ammonia, and gelatinous silica.

Pereles :<sup>2</sup>—Combined solutions of sodium phosphate, silicate, and tungstate.

Nicoll :<sup>2</sup>—Solution of alum, borax, sodium tungstate, and dextrin, or equal weights of calcium acetate and chloride in hot water.

These comprise the processes for the protection of fabrics introduced up to the present time. As is easily seen, the use of sodium tungstate, the borates, or ammonium salts alone or in mixtures is the striking feature.

<sup>1</sup> *Génie civ.*, 6, 227.

<sup>2</sup> *Sc. Amer. Cyclop. of Receipts*, p. 217.

A few words with regard to the methods of manufacturing or protecting paper are here in place.

Martin and Tessier<sup>1</sup> used the following bath for paper whether printed or unprinted.

Ammonium sulphate...	8	parts.
Boric acid.....	3	"
Borax.....	1.7	"
Water.....	100	"

The solution is placed in a vat, at the end of the paper-making machine and kept at 50° C.

Paper thus treated is non-inflammable. The value in many kinds of business of a totally incombustible paper is easily appreciated; and several varieties, all based on a large use of asbestos, are in vogue. L. Frobeen's paper is made from ninety-five per cent. of asbestos and five per cent. of wood-pulp mixed in water containing borax and glue. For ink he uses a mixture of platinum chloride and india ink.

Halfpennig's paper<sup>1</sup> is made from one part vegetable fiber, two parts asbestos, one-tenth part borax, and one-fifth part alum, formed in the ordinary way into a pulp to which waterglass is sometimes added. A paper of great flexibility and strength is obtained by coating sheets of linen on both sides with the incombustible paper. His ink is a mixture of graphite, copal, copperas, and indigo sulphate.

Paper is also made from pure asbestos and from asbestos mixed with alum, aluminum sulphate, zinc chloride, and resin soap.

A fire-proof writing-ink is an ammoniacal solution of silver nitrate, with a little india-ink, while platinum chloride mixed with lamp-black and varnish is employed as a fire-proof printing-ink.<sup>1</sup>

#### METHODS FOR RENDERING WOOD INFLAMMABLE.

In taking up next, the history of the efforts to render wood non-inflammable we encounter two distinct methods of procedure. The first is impregnation by the solutions of the chemical compounds which are to be operative, and includes such variations as the precipitation of insoluble salts within the wood by double

<sup>1</sup> Sc. Amer. Cyclop. of Receipts, p. 217.

decomposition; the second is the covering of the exterior of wood by protective coatings. In the case of existing structures, the latter is evidently the only means available.

The first recorded effort to protect wood was made at Munich in 1823, during the rebuilding of the Royal opera house after destruction by fire.<sup>1</sup> On the recommendation of Professor Fuchs all of the woodwork then received several coatings of waterglass. The surface covered was 400,000 square feet, and the cost was \$1,000, or at the rate of \$1 for 400 feet. Professor Fuchs prepared his solution by treating ten parts of caustic alkali, fifteen parts of infusorial earth, and one part of charcoal, with water. A somewhat similar composition was also in vogue then in England. It was made by grinding in oil one part of fine sand, two parts of wood-ashes, and three parts of slaked lime, and was applied with a brush. Fuchs' protective kept well, and was regarded as effective for twenty years, but later tests showed that its chemical composition was materially changed, and it no longer afforded security. It may be mentioned here that it was not then found available for scenery on account of the gloss it imparted. During this period the following mixtures came into vogue, chiefly for external protection, as in the case of shingled roofs: three parts of wood-ashes and one part of boiled linseed-oil; three parts of alum and one part of copperas; ashes and lime with skimmed milk as a binding material.

In 1841 Payn<sup>2</sup> introduced his combined process for rendering wood not only unflammable, but also proof against wet and dry rot and insects. It consisted in the precipitation throughout the mass of a piece of timber, of barium or calcium sulphate by double decomposition. In carrying out the process, wood is introduced into a capacious cylinder, the air is drawn out by steam, and a solution of barium or calcium sulphide is injected into the partial vacuum; the cylinder is exhausted again and then completely filled with the solution of the sulphide; pressure is increased to 140 pounds per square inch, and after an hour the solution is drawn off. The operation is then repeated, use being made of a solution of copperas; as a result the pores of the wood are largely

<sup>1</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885; Hexamer, *Jour. of the Frank. Inst.*, 114, 125.

<sup>2</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

filled with the insoluble sulphate and it becomes hard as stone. The soft, porous, cheaper grades of wood are thus rendered equal in point of durability and strength to the hardest varieties of timber. Wood prepared in this way is largely used in England in connection with public works and railways.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, NO. 12.]

## NOTE ON THE ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES.<sup>1</sup>

By K. P. MCELROY.

Received January 8, 1895.

IN 1888 Dr. Crampton, then First Assistant Chemist of the United States Department of Agriculture, was engaged in the analysis of a lot of baking-powders and did me the honor to entrust to me a portion of the analytical work. Among other things I had to determine the alumina in a number of alum phosphate powders and met with the usual difficulties. By the method I was instructed to use, I found it impossible to get results that were concordant. I therefore systematically went through all the known methods for separating alumina from phosphoric acid and finally decided to use the one accredited to Mr. T. R. Ogilvie in Crookes' Select Methods (page 538, edition of 1886). Briefly stated the method consists in neutralizing the filtrate from the phosphomolybdate precipitate with ammonia, redissolving the precipitate of mixed sesquioxides thus formed, in nitric acid, once more precipitating, filtering, burning, and weighing. The process gave very good duplicate results, and a trial with a known amount of alumina in the form of alum mixed with sodium phosphate gave results sufficiently near theory. This, together with the fact of its having appeared in a work so standard as that of Crookes, seemed sufficient credentials for the method, and I placidly went ahead with its use. When Dr. Crampton prepared his manuscript (which I did not see prior to publication) for his bulletin on baking-powders (Bulletin 13, Part Five, Division of Chemistry, U. S. Department of Agriculture) he gave me credit for the minor modifications I had made

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.



in the method, such as getting the alumina into solution, making up to volume, and the like. As to the main part of the method, the precipitation of alumina by ammonia in presence of molybdate solution, he had as little intention of accrediting it to me as I had of claiming it. He simply said (page 595) that the method "was adapted to the powders by Mr. K. P. McElroy."

Several years later Mr. W. H. Krug of this laboratory was engaged in making an exhaustive examination of a number of phosphate samples and had considerable trouble in determining iron and aluminum. In this connection he tried a number of the current methods on synthetic solutions and got results not agreeing with each other or with theory. At this juncture I suggested that he try the molybdate method. He used it on some phosphates which he had previously examined by the Glaser, Stutzer, etc., methods and obtained much better results. Subsequently he published a paper (*J. Anal. Appl. Chem.*, 1891, 5, 671) detailing his work and incidentally he courteously acknowledged my suggestion by saying of the molybdate method that it "was first used in this laboratory by Mr. K. P. McElroy for the estimation of alumina in phosphatic baking-powders." I had also suggested to Mr. Krug some modifications differing in minor detail from those of Ogilvie, by which it would be possible to determine calcium and magnesium in the same portion after precipitation of the iron and aluminum, and these Mr. Krug also published giving me full credit.

For some time since I have known that various chemists had fallen into the habit of calling this method for ferric oxide alumina, the "McElroy method" or "Krug method." Neither of us has taken the trouble to correct this mistake except orally since Crookes' *Select Methods* is a book of nearly as frequent occurrence in chemical laboratories as Fresenius' *Quantitative Analysis*, and publishing such a denial of authorship seemed nearly as ridiculous as it would be for one of us to rush into print to announce that he was not the originator of the method for the estimation of sulphuric acid as barium sulphate. Recently, however, a Northern chemist wrote a letter to the Department of Agriculture, designating the method by my name and announcing that in the case of a certain phosphate rock the method had

failed to give results concordant with those of other chemists using other methods. I had always known that the molybdate method did not give results agreeing very closely with those of other methods, but as I had also known that most of these other methods gave incorrect results, I had not laid the fact up against the molybdate method. In view of this specific complaint, however, I have tried the method on known solutions and am astonished to find that it really is liable to lead to grave error.

In this work I tried several samples of the molybdate solutions prepared according to the directions of the Association of Official Agricultural Chemists, which happened to be in the laboratory and found that they gave varying results. The worst results were obtained with a solution made up about six months ago, from which a heavy crystallization has taken place, leaving the residual liquid so weak that it requires over 100 cc. to precipitate the amount of phosphoric acid supposed to be thrown down by fifty cc. of a fresh solution. In two beakers I placed portions of ferrous sulphate representing each 56.4 mgms. of ferric oxide, added a solution of sodium phosphate representing 100 mgms. of phosphorus pentoxide to each, brought into solution in weak nitric acid, oxidized with bromine water, and then precipitated with the molybdate. I washed the precipitate with weak nitric acid and neutralized the combined filtrate and washings with ammonia. The resultant precipitate was dissolved in a solution of ammonium nitrate and nitric acid, filtered, and again thrown down. This precipitate was collected on a filter, burnt, and weighed. The amount recovered was respectively 56.9 and 57.3 mgms., showing a small plus error. In a duplicate set of experiments calcium nitrate equivalent to 400 mgms. of calcium oxide was added to each of the initial solutions. The amount of precipitate recovered in one case was 62.3 mgms. and in another 63.1 mgms., showing a large plus error. During the first precipitation a heavy white crystalline deposit of calcium molybdate occurred. The weighed precipitate was found to contain both lime and molybdic acid, showing that the same phenomenon had occurred in the second precipitation, though it was not visible to the eye.

In each of two beakers were next placed 35.6 mgms. of

alumina in the form of ammonia alum, together with 100 mgms. of phosphorus pentoxide in the form of sodium phosphate and the mixture treated as were those containing iron. The two precipitates of aluminum oxide finally obtained, weighed respectively 28.9 and 29.3 mgms., showing a large minus error. Another set containing 400 mgms. of lime was run through. The same precipitation of calcium molybdate was found to occur. The weights of alumina obtained were but 19.8 and 20.6 mgms. respectively, showing a much larger minus error.

From the above surprisingly bad results it is shown conclusively that the molybdate method for iron oxide and alumina, at least in this form is not at all trustworthy. Yet I have myself at times, and so have others, obtained good results by its use where these results were checked against those made by some of the standard methods used in delicate work.

### SOME PRACTICAL POINTS IN THE MANUFACTURE OF NITROGLYCEROL.<sup>1</sup>

BY J. E. BLOMEN, PH.D.

Received January 2, 1895.

FROM the very beginning of the commercial manufacture of nitroglycerol the aim of the inventors and manufacturers has been to eliminate the dangers of the operation to the highest possible extent and they have been so successful in this that very few, if any of the many accidents on record can be traced back to the apparatus. The problem is simple enough as the reaction is easily controlled. The indications of approaching danger are clear and the means to avoid it are easily kept at hand. From the old wooden boxes worked by hand with a paddle-wheel to the present elaborate apparatus, the principle is the same—to secure an even and low temperature through the mass of the mixture of acids and nitroglycerol.

It has long been considered that the safest way of stirring is with compressed air, but this can hardly be taken as an axiom. The water, which is formed during the reaction, is of the same temperature as the mixture and does not tend to elevate the temperature, but the moisture brought in with the air certainly does

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.

raise the temperature as soon as it comes in contact with the acid. To prove this point air of the temperature of  $82^{\circ}\text{F.}$  was passed for five hours through a mixture of nitroglycerol acids (three-fifths sulphuric acid to two-fifths nitric acid) of  $86^{\circ}$  for five hours. After thirty minutes the temperature had risen to  $92^{\circ}$ , after one hour to  $93\frac{1}{2}^{\circ}$ , after two hours to  $94^{\circ}$ , after three hours to  $94\frac{3}{4}^{\circ}$ , after four hours to  $95\frac{1}{2}^{\circ}$ , and after five hours to  $95\frac{3}{4}^{\circ}$ , the temperature of the air remaining constant and the barometric pressure being 762 mm. during the entire experiment.

The apparatus is necessarily far away from the air-compressor and the air therefor has to be carried in pipes for a considerable distance. If then, as frequently happens, the moisture of the air (when not used for stirring) is condensed a considerable quantity of water is forced into the said mixture at one time and it becomes difficult to control the apparatus. Besides a stoppage in the pipe-line may take place at any time—for instance from a bad leakage, from an ice-plug or other substances in a pipe-section, or something may suddenly happen to the air-compressor. For these reasons it is doubtful if this system has any advantage over a stirrer or serpentine screw operated by an engine close at hand and which can be supervised by the operator. The latter way is besides decidedly the more economical as the moisture in the air (most of which comes in at the beginning of the operation) tends to dilute the acid mixture at the time when it is most important that the latter should be as strong as possible and the continuous forcing of warm air through nitric acid cannot but weaken this to a considerable extent.

It is true that when air is used the cooling surface can be better distributed by means of a number of smaller coils through the whole apparatus, but quite sufficient cooling surface is obtained by one big coil (embracing the serpentine screw or paddle-stirrer) when the mixture of the nitroglycerol acids is continually thrown against this and the sides of the apparatus cooled off by a water-jacket.

The question of how big a charge should be used at one time has been a matter of considerable controversy between expert nitroglycerol manufacturers. Of course it would be of the greatest advantage and convenience to use an apparatus big enough

to make one day's output of nitroglycerol in one operation, but this is hardly practical. It seems to be the experience of manufacturing chemists that very few chemical reactions can be effected with advantage on a very large scale; the nearer the operations come to the laboratory conditions the better is the result. This maxim is particularly true in this case. The dilution of the acids by the water formed is considerable— $C_3H_5-O_2H + 3(H-O-NO_2) = C_3H_5-O_2-(NO_2)_3 + 3H_2O$ —and the acid mixture is consequently rapidly weakened. This cannot but have a serious effect on the reaction and if a very big charge is operated the acid mixture necessarily becomes uneconomical in composition. If air is used for stirring, of course, that will also weaken the mixture the longer it is used. Furthermore the acids will always find some little nook or corner of the apparatus—be this of lead or iron—that is weak and in a short time it will act upon it so that the apparatus must be repaired or renewed, and if it then is very big, the trouble and cost this will cause is obvious. Besides, if a charge should need to be drowned, as will happen, the loss is heavy.

On the other hand a charge should not be made too small, because it would take too much time and labor to cool off the acid mixture and rearrange the operation. A convenient charge to operate is one that will take one drum of the acid at a time. One drum holds about (or can by contract be made to hold exactly) 1,500 pounds of mixed acids. Experience has shown that the best composition of acids is three-fifths of the strongest sulphuric acid to two-fifths of the strongest possible nitric acid and 1,500 pounds of this mixture will nearly fill an ordinary iron drum. It has further been proved that it takes a little more than seven pounds of this mixture to each pound of glycerol to obtain a good yield of nitroglycerol. If therefore the apparatus is constructed for a charge of one drum (1,500 pounds) mixed acids and 210 pounds glycerol, it seems to meet the requirements of both practical and theoretical conditions. Of course, the size of the apparatus has to be such as not to allow any undue pressure to be exerted on the charge by confining the mixture and not so large as to allow a play of waste acid fumes to attack a large surface on the top portion of the apparatus.

Of late some so-called continuous apparatus have been proposed. I have never seen one in operation and cannot judge of their practicability. Knowing, however, how difficult it is to get the acid mixture uniform (on account of stratification of the acids), I doubt if they prove economical. If the jets of glycerol and acid mixture meet it is of the utmost importance that the latter should be of uniform composition and the difficulty of getting it so is within the experience of every manufacturer of nitroglycerol. If the acid is not continually stirred it will lack uniformity, and give a low yield, the temperature will fluctuate to a great extent and the danger of the manipulation will be greatly increased. Besides a small jet is easily stopped up and then in a few seconds the point of safety is overstepped.

#### SEPARATORS.

Formerly, when the cost of the nitroglycerol was of less importance; the nuisance of strongly acidulated water was not considered; and the yield was not all important; the charge was always drowned immediately after it was made. Now it is necessary to recover the "spent" acids, both for the reason of economy and so as to avoid the accumulation of acids, which otherwise would destroy whole tracts of land. On a small scale, when the apparatus only has to be used two or three times a day, it can also be used as a separator, but usually this is not the case, and such a number of separators has to be used as will permit the first one being emptied while the last one is being charged. For this reason the size of a separator ought to be such that it will hold exactly one charge of the converter.

The forms of separators have varied from that of a square box to that of a cylinder and a funnel. As they are generally made of heavy lead it is of advantage to present as few seams and corners as possible, and for this reason they should be made round so that only one seam is necessary. The funnel-shaped undoubtedly possesses several advantages, such as easy separation, but it takes too much space and must be made too deep to be convenient, if the nitroglycerol is to be skimmed off. An ordinary wooden tub, lined with heavy lead (ten pounds to the square foot), which at the bottom has an inclination of about six inches, or is drawn to a funnel-shape, answers the purpose very well.

The faucets of the separators, as well as of the apparatus, ought to be of earthenware, perfectly ground and well greased with vaseline, but the place to put them is hard to determine. The separation line of the nitroglycerol from the acids, varies considerably, partly on account of the difference in yield and partly because the amount of acid used frequently varies from three to four inches.

If the upper funnel be too high up it frequently happens that several inches of nitroglycerol remain and have to be dipped, and if it be too low the amount of acid drawn off would be a source of danger in the wash-house. If the charge is not too big the "dipping off" is accomplished in a short time and the constant stirring of the dipping pan (an enameled iron casserole) in the nitroglycerol helps the separation considerably. It is, however, necessary to have an experienced man in the separating room as the greatest loss is here, if the skimming is not conducted with the most scrupulous care. In most cases it is preferable to dip besides having faucets as every one of them, being brittle as they are, considerably increase the danger from breaking. The separation ought to be accomplished in an hour and a half. If it is not, the glycerol used has been inferior or the operation in the apparatus has been faulty. If the glycerol contains calcium or other alkaline salts and fatty acids there will be found a great number of worm-like particles floating up and down, mechanically carrying nitroglycerol to the acids and *vice versa*, and the charge had better be drowned. The last two inches in the separator should be drowned as it always contains enough acid to considerably raise the temperature of the first wash-water and here is where the funnel, the spout, or the inclined bottom is of advantage as it only allows a narrow separating belt. If the charge is run down in the separator at  $17^{\circ}$  to  $19^{\circ}$  C., it scarcely, if ever happens that the temperature rises again to any dangerous degree. It is indeed very rare that it happens that the temperature varies to a dangerous degree in the separators, but it is of the utmost importance to guard against such an occurrence and it ought to be made compulsory for the man in charge to note down the temperature registered at the thermometers in each separator every fifteen minutes, and any neglect

or omission in this respect should be followed by immediate dismissal, as it possibly endangers the life of every one connected with the manufacture.

Before the charge is allowed to leave the separator-house it should be immersed in, and for a few minutes stirred, with cold water, both for the reason of security and economy; of security, because the nitroglycerol mixed with even a small quantity of acid is liable to explode in the pipes in case a friction should take place, or some water be present to raise the temperature of the adherent acid and of economy, because the first wash-water will invariably carry along some nitroglycerol, which ought to go to the drowning tank where it will settle at the bottom of the tank.

#### WASH-HOUSE.

When it is considered how very important a thorough washing of the nitroglycerol is, what danger a poorly or insufficiently washed nitroglycerol is in the process of manufacture, and that it is an ever-increasing source of danger the longer it is stored, the question of a proper wash-house is one of great importance. As to the form of wash-tubs, the conical one is undoubtedly the best. This form admits the broadest possible surface of contact, it prevents any water coming with the nitroglycerol when it is drawn off, and affords a good opportunity for skimming or drawing off the wash-water. The size need not be larger than to easily accommodate one-half of the charge, because the man who washes has plenty of time to do this when the charges are settling. The wash-tubs as well as the faucets can be of wood (preferably cedar), which should be free from knot-holes, as so little acid comes along when a charge is well separated and has had a preliminary washing in the separator-house that it cannot attack the wood. When a charge is let down the water ought to be let down slowly and from a coil at the side of the wash-tub so as to give it an opportunity to bubble through the nitroglycerol.

If compressed air is to be had, that is, of course, the preferable stirrer, otherwise wooden stirrers can well be used. To prevent waste the wash-water, when drawn off, ought to be allowed to stand in a big tank as it always carries some nitroglycerol along, which will be deposited at the bottom of the tank and should be



taken out at least once a week. The amount of water to be used depends, of course, upon the size of the charge, but twice the volume of the nitroglycerol is certainly enough under all circumstances. If the charge has been well separated and a preliminary washing has been given it one washing will be enough. The last trace of acid should now be taken out. For this purpose a weak alkali solution is used. It is a convenient arrangement to have this solution in a tub set up somewhat higher than the wash-tub and let it run in by gravity, preferably through the coil which is used for the wash-water. If the water in this tub is kept at 30° to 35° C. and the water at this temperature is nearly saturated with sal-soda or if about five pounds of soda-ash are used to about fifty gallons of water the solution is of proper strength. Of this solution I have found that it takes about two pails to remove the last traces of acid in about 460 pounds of nitroglycerol. After the soda solution is drawn off the nitroglycerol should have one thorough washing with water and then it ought to be ready for use. To ascertain this, however, each and every charge should be tested. This of course can be done with any one of the ordinary indicators and the choice of one depends upon the intelligence and education of the man in charge of the washing. For any ordinary workman I would recommend the use of very carefully prepared litmus paper. This is more easily handled than most indicators and is quite sensitive. It must be kept in well-corked bottles and out of the acid fumes. The liquid indicators generally require more skill than the man in charge can be depended on to exercise. Two like strips of litmus paper should be used at one time, one dipped in a little distilled water (which the steam on hand always can furnish) and the other in the nitroglycerol and then be compared. When the wash-water tank is cleaned it will be found that a spongy, dark-gray substance has accumulated. This consists chiefly of salts from alkalies and fatty acids, and holds mechanically a good deal of nitroglycerol. To get this out a felt filter can be used, and by letting it stand long enough in this a good deal of nitroglycerol is obtained.

It is difficult to give a rule for the size of the drowning-tank. This depends upon the size of the converter and the charge used ;

the amount and composition of the acid mixture; the size of the separators and somewhat on the temperature of the water available. It must be large enough to allow one full charge to be drowned without the least danger. It would seem as if the larger the tank the greater the safety, but that is not so. If the tank is very big the very large amount of water it holds exerts a pressure, which is likely to spring either the bottom staves or the sides, or the faucets, and if this is done and the acidulated nitroglycerol comes in a crevice not reached by the water, it immediately attacks the wood, generating a heat which sets the nitroglycerol afire and the danger is considerable. It is hard to empty and clean a very large tank; such a tank will last a shorter time than a smaller one, and when it is to be replaced the cost is considerable and the time required, during which the manufacture must cease, is long. On the other hand, if the tank is too small, it is dangerous to drown a full charge; the water in the tank is always strongly acidulated from the last inches of the separators, which must be drowned and is consequently hard to dispose of and constant and tedious cleanings must be made. With these points in view it seems to me to be the best arrangement to have two medium-sized tanks for drowning-tubs connected in such a way that they are in constant communication but will allow each one to be disconnected from the other and connected with the apparatus, separators, and wash-house separately. The size of each one need then only be such that one alone will be enough for an emergency during the short time required to repair the other.

To ascertain the cost of the powder, to be able to check the carefulness of the men, and to rightly regulate the daily output it is of importance that the yield of nitroglycerol and the amount on hand can be easily ascertained at any time. I have found it convenient for this purpose to have the storage tank placed on a large platform scale, where it can be weighed at any time. It is weighed, the amount of nitroglycerol taken out since the last weighing is calculated from the formulas of the powder produced; the weight of tank and nitroglycerol at previous weighing deducted; and this amount divided by the number of charges run down; an average yield will thus be had. The storage tank

—to fit the platform scale—should be a square lead-lined box, and of such a size that it will hold enough nitroglycerol for the manufacture of high-grade dynamite even if three charges should be delayed in converter, separators, or wash-house.

I have found it most convenient to draw the nitroglycerol from the storage tank by means of a rubber hose long enough to reach the top of the tank when raised. If this hose be fastened by a clamp to the upper part of the tank it will not be necessary to have a faucet which must be turned every time a bucket is drawn and which is likely to give rise to considerable friction. By bending the hose sharply between both hands the nitroglycerol will be shut off until the end of the hose reaches the bucket, placed on a small platform scale some distance away, when it can be let down carefully in any desired stream simply by relieving the pressure. The mouth of the hose should, of course, be carefully wiped off before being put back into position.

The problem of conveying the nitroglycerol in the most careful manner from one house to another and from the storage-tank to the mixing-house is one that is astonishingly neglected in most powder works and yet it is one of the utmost importance. It is imperative that no communication by hose, pipes, or trays should exist between the buildings except during the time actually taken to run a charge from one to the other. In case of explosion or fire in one of the buildings the whole factory is doomed to destruction if connections exist between the buildings, but if the connections are cut off the plant can, without difficulty, be so constructed as to make one building independent of the other, as Professor Munroe's valuable experiments have clearly shown, that nitroglycerol is less liable to sympathetic explosion than was generally considered. The converter should be in direct communication with the drowing-tank, and not be allowed, as is so very frequently the case, to communicate with this by the way of the separating-house. This connection may be permanent as the danger of explosion in the drowing-tank is small, but for the sake of additional safety, may be broken near the apparatus. The connection between the apparatus and the separating-house may be made either of lead pipes or rubber hose, but in both cases it should be broken off at an equal distance

from both buildings, a space of at least twelve feet allowed between the ends of the pipes or hose, connection being made between the ends only when a charge is let down and disconnected as soon as the charge is down, and the upper end should terminate in a small lead-lined box to receive drippings. The same conditions should be observed between the separating-house and wash-house, and between the wash-house and storage-tank, and any failure to immediately disconnect the line after use should be severely reprimanded and repetition followed by dismissal. The connecting and disconnecting can be very easily accomplished by a piece of rubber hose and two short glass tubes.

To convey the nitroglycerol from the storage-tank to the mixing-houses pails are almost invariably used. These pails were formerly either of lead or of leather but indurated fiber buckets may be used, if precaution is taken to tare the buckets at least once a week since they are affected to a certain extent by the nitroglycerol.

It is necessary that the nitroglycerol plant with the storage-tank be kept at a considerable distance from the mixing or dynamite manufacturing plant and consequently these buckets have to be carried a long way. The rule not to have any connections between the houses is still more forcible when the connection between the storage-tank and the mixing-houses is considered; no pipe line between the plants should be admissible. In most cases the men have to carry these buckets by hand and a close supervision should be kept to ascertain that the men are careful in doing this, especially in slippery weather. Acting on the suggestion of Professor Munroe some three years ago Messrs. Roebling & Sons built a trolley system to carry the nitroglycerol from the storage-tank to five different mixing-houses at the Forcite Powder Manufacturing Co.'s plant, in Hopatcong, N. J., and this plant worked perfectly satisfactory.

In the construction of a nitroglycerol plant it has always been maintained that it should be so located that the nitroglycerol may run down by gravitation from the converter to the storage-tank. It is well and good if this can be done without inconvenience but it is in no way any absolute necessity, as it can easily

be arranged to press the nitroglycerol from one building to another with compressed air without any great cost and with perfect safety. The mixed acids should, if possible, be cooled off for some time in a place higher than the top of the converter, and if the time it takes to run a charge is allowed for in cooling the acids for the subsequent charge they will not need to be cooled off in the converter, which would otherwise delay the running, considerably. As the glycerol almost invariably has to be warmed before using to assure an even flow and as this operation can easily be done in the converter-house, it is necessary to afterwards press up the glycerol required to a receiver above the apparatus.

The safe distance between the buildings depends partly upon the nature of the ground, partly upon the amount kept in a building at one time, and partly upon the construction of the buildings themselves. The drowning-tank should be as near the converting-house and the separating-house as possible and so low as to assure the rapid discharge of a charge. If the ground is hard the shock of an explosion is more easily carried from one building to another than if it is soft or marshy and the buildings have then to be further apart. If the nature of the ground allows a natural protection of one house from another, or if artificial banks can be built between and at some distance from the houses the latter can, of course, be closer than when unprotected. The buildings ought to be constructed in the lightest possible manner so as to afford little resistance to an explosion, which would otherwise be too powerful. All the buildings must be ceiled and in every way so protected as to assure as even a temperature as possible, but the foundation, the framework, the roof, etc., can be of a very light material. In the separating-house, as well as in the wash-house it is to be recommended that the floor be lined with lead, as this materially assists in keeping the house scrupulously clean and prevents any acidulated nitroglycerol from creeping in between joints, a thing that must be carefully avoided.

To obtain a good yield of nitroglycerol, that is, to make powder economically, the materials selected must be of the best quality or rather of the most suitable quality for the purpose.

To obtain and maintain this there is only one way open to the manufacture; *viz.*, to let a chemist of experience and standing draw up specifications for the acid mixture and the glycerol and to employ a chemist to see that the specifications are rigidly enforced. Some of the more prominent powder works in this country have now such specifications drawn and it would be of great benefit to the trade in general if they should be published so as to lay down a normal rule for the contractors. In this connection I wish to state that whenever it is practicable it is, without doubt, the most economical and best plan for dynamite works to make their own nitric acid. The iron drums, in which the acid mixture comes, are not affected by sulphuric acid but no one ever claimed that they are not affected by nitric acid, and it is hard to see why this should not be the case even when the nitric acid is mixed up with the sulphuric as it can hardly be claimed that the sulphuric acid is a preventive against such attack. It is so frequently lost sight of by manufacturers that the sulphuric and nitric acids are simply a mechanical mixture in which each one retains its peculiar chemical properties, and not a compound different from anything else. This mixture stratifies by standing, the nitric acid corrodes the drums, which are consequently weakened, and, worst of all, it may not be uniform in composition. The contractors frequently mix the acid in tanks in sufficient quantity to fill two or three car-loads. This mixture, which is drawn from the tanks to the drums, must, by necessity, be lacking in uniformity as the specific gravity of the sulphuric acid is so much higher than that of the nitric. It has come within my experience that when the supply of acid mixture was delivered at the beginning of the month instead of being distributed in weekly deliverances, the acid mixture in the drums which have been lying for four weeks has been very much inferior to that which was used in the beginning of the month and that consequently a bad yield resulted. If there were no other reason existing than that of getting a uniform mixture of acids it would be sufficient to advocate the erection of a nitric acid plant, but besides that it is decidedly more economical to have such a plant and it makes the manufacturer more independent both of contractors and of freight service.

To test the stratification of the acid mixture some glass jars four feet high and four inches in diameter were filled with an acid mixture of sixty-five per cent. sulphuric acid to thirty-five per cent. nitric acid and the mixture allowed to stand undisturbed for some time. In four days the color of the upper four to five inches had changed from a pale yellow to a brown color. After six days standing a sample taken six inches from the top had the composition of thirty-eight per cent. nitric acid and sixty-one per cent. sulphuric acid, and after twelve days an analysis gave thirty-nine per cent. nitric acid and 58.4 per cent. sulphuric acid. A sample taken at the bottom of a jar after six days standing gave sixty-eight per cent. of sulphuric acid and thirty-two per cent. of nitric acid, and after twelve days such a sample gave seventy per cent. of sulphuric acid and 29.3 per cent. of nitric acid. These figures represent the average of a number of analyses.

What is to be done with the spent acids and where to run the acidulated water from the drowning-tank and the wash-house are questions which well deserve attention. There exist at present three ways of using the "waste" acids each one of which has some merits. In Europe these acids are most frequently used for the manufacture of fertilizers. Where other fertilizing materials are scarce and insoluble phosphates are plentiful it is natural that the use of this acid for the conversion to soluble phosphate should flourish. The most usual way to utilize the "spent" acid in the United States has hitherto been to "regain" it. The ordinary way of doing this has been to pass the acid mixture through towers filled with coke or bricks where it is met by a jet of steam, which carries the nitric acid through the top of the tower and to receivers, leaving the sulphuric acid to run down to the bottom. The waste of this process is obvious. The sulphuric acid is diluted to such a degree as to make it almost valueless, and the nitric acid rarely acquires a strength of more than  $32^{\circ}$  to  $34^{\circ}$  B. The acids in the waste acid mixture has still considerable strength, and to dilute them in order to "regain" them is uneconomical. The third way is to use the mixture direct for the production of nitric acid. It contains nitric acid of the strongest kind, as all the water formed during the reaction has

been taken up by the sulphuric acid, and the sulphuric acid itself has not been diluted to such a degree that it is unsuited for nitric acid manufacture. If the mixed acids, therefore, be added to a charge of sodium nitrate and strong sulphuric acid, almost all of the nitric acid will be recovered. The objection always raised to this plan is that the mixture may contain some traces of nitroglycerol, which would endanger the process. In answer to this it can be said, first, that very little nitroglycerol need be present if the separation has been carefully conducted, and if the acid has been allowed to stand (preferably cooled) for some time before using; secondly, that the very small amount remaining can be exploded by detonating a strong cap in the vessel in which it is stored before using; and thirdly, that even if present in a considerable degree in the retort it would all be decomposed there by the sulphides formed, which are the best decomposers of nitroglycerol known. This way of utilizing the "waste" acid is one of the most economical that can be devised. Unfortunately, however, it only applies to factories having nitric acid works of their own. If the waste acid is kept in iron vessels with free access of air, the vessel will soon be attacked, but if the air is excluded it is not affected. I was brought to this conclusion by observing acid drums a few years ago and to ascertain how far this was true the following experiment was carried on: A small iron still, previously weighed and heated with an iron coil was filled to two-thirds with "waste" acids and connected with a vacuum pump. The acids were now boiled down to about one-half of the still by steam-heat in vacuo. The acid was tested and it was found that the sulphuric acid was of sufficient strength for immediate use and the nitric acid was as strong as before using, but about twenty-four per cent. of the original acid was gone. By adding strong nitric acid to this mixture in such amount as to re-establish the proportion between sulphuric and nitric acids the acid may be directly used again. The still had, after repeated use, lost almost nothing in weight, showing that it was not affected by the acids under this condition. Continued experiments in this direction may give a solution to the problem of how to economically use the waste acids in works which have no nitric acid plant. To pay freight for a strong



nitric acid, use part of it, dilute the rest, and pay another freight back to the factory from where it came, as is done where regaining works are used is certainly not economy.

The acidulated water from the drowning-tanks, wash-house, etc., is frequently a source of great annoyance to the nitroglycerol manufacturers. It cannot be let down into running water as it will soon pollute this; it cannot be run into the field as it will soon destroy all vegetation and cause complaint from all sources. If a deep ravine, separated by considerable earth banks from water supplies is to be found on the ground it may be run into that. The ravine, however, ought to be thoroughly cleaned from leaves, etc., and the bottom scraped so as to enable the soil to absorb the water quickly. If limestone of any kind is to be had on the grounds or near by it is certainly the best way to blast a big excavation, fill it with the limestone, and let the wash-water run into this. The limestone will purify the water from adherent nitric and sulphuric acids and affords a good drain for the water.

How far the risks of the dangerous manufacture of nitroglycerol can be minimized may be judged by the fact that since 1871 no accident of any kind, explosion, or fire has taken place at Winterwiken, Stockholm, Sweden. What is of the utmost importance is to have well-constructed plants, good supervision, and a good chemical knowledge.

COLUMBIAN UNIVERSITY,  
December, 1894.

## METHODS FOR THE EXAMINATION OF GLYCEROL FOR USE IN THE NITROGLYCEROL MANUFACTURE.<sup>1</sup>

BY G. E. BARTON.

Received January 2, 1895.

THE most commonly accepted methods for the examination of glycerol are described by Allen in his *Commercial Organic Analysis*, Vol. II.

His requirements are very severe, in fact, too severe it seems to me in some respects. For example, he requires entire freedom from chlorides and iron. Most of the glycerol offered to the

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

nitroglycerol trade contains both these impurities and, in limited amounts, they are not harmful. He also requires only feeble reaction with basic lead acetate, yet distilled water gives a decided reaction with this reagent.

It is not possible, using the methods of examination Allen gives, to accurately describe a glycerol suitable for the manufacture of nitroglycerol.

The different impurities that such glycerol is liable to contain are:

1. Inorganic bodies, other than sodium chloride, which are shown accurately enough for technical purposes by the ash determination.
2. Sodium chloride.
3. Carbohydrates, sometimes used as adulterants, which are shown by the carbonaceous residue.
4. Fatty acids, either free or combined, a measure for which is found in the total acid equivalent or saponification number.
5. Lighter bodies, mainly hydrocarbons, which influence the permanent specific gravity quantitatively.

The following methods of examination are the result of several years' experience in the examination of glycerol intended for use in the manufacture of nitroglycerol.

*Ash and Carbonaceous Residue.*—Weigh out between four and one-half and five and one-half grams of glycerol in a tared porcelain capsule and heat cautiously till it inflames. Remove the source of heat and allow it to burn away. Transfer the capsule to a desiccator and, when cold, weigh. This gives the weight of the carbonaceous residue.

The carbonaceous residue ignited gives the ash.

*Sodium Chloride.*—Take 100 cc. of glycerol, transfer to a porcelain casserole, rinse with distilled water, and add the rinsings to the contents of the casserole. Dilute to 300 cc., neutralize any free acid with sodium carbonate, add normal potassium chromate solution till the contents of the casserole have a decided yellow color, and titrate with tenth normal silver nitrate solution. After deducting two-tenths cc. required to give the coloration, the remainder is calculated to sodium chloride. The weight of glycerol taken is calculated from the number of cubic

centimeters, using the specific gravity at the temperature of the room.

*Total Acid Equivalent.*—One hundred cc. of glycerol are taken for the determination, transferred to a beaker, made up to about 300 cc., a few drops of a one per cent. solution of alcoholic phenolphthalein added, and then ten cc. of normal sodium hydroxide. Boil for a short time and then run in normal hydrochloric acid till the pink color is discharged. The result is expressed in grams of sodium hydroxide required by 100 cc. of glycerol.

*Higher Fatty Acids.*—Pass a stream of nitrogen tetroxide through a portion of the glycerol diluted with twice its volume of distilled water, then heat on a steam-bath for two hours. If there is no precipitate formed, either on diluting or later in the operation, the glycerol may be considered free from higher fatty acids. Glycerol intended for use in the manufacture of nitroglycerol should stand this test.

*Neutrality.*—A glycerol may be considered neutral if, when fifty cc. are diluted with 100 cc. of water and a few drops of an alcoholic solution of phenolphthalein added, not more than three-tenths cc. of normal hydrochloric acid or normal sodium hydroxide solution is required to produce the change in color.

*Specific Gravity.*—For the specific gravity determination, a Sartorius specific gravity balance is used, and the determination is made at the temperature of the room. The value found is reduced to the value at 15° C. by adding a product represented by  $(t-15)$ , 0.00065 and subtracting from this sum a number represented by  $0.0003 + (t-15) 0.000025$  R, when  $t$  is the temperature at which the work is done, read from a thermometer in the glycerol, and R is the value read from the balance.

*Permanent Specific Gravity.*—Heat a sufficient portion of glycerol for a specific gravity determination in a 250 cc. flask for two hours, at a temperature between 225° and 230° C. At the end of this time allow the glycerol to come to the temperature of the room, keeping the flask corked with a stopper having a small opening for equalizing the pressure. The specific gravity is then determined as before described. The result is the permanent specific gravity at 15° C.

A good sample for nitroglycerol purposes tested as follows: ash, trace; carbonaceous residue, 0.012 per cent.; sodium chloride, 0.002 per cent.; total acid equivalent, 0.05347; permanent specific gravity, 1.2653; specific gravity, 1.2634; higher fatty acids, none; reaction, neutral.

I am indebted to Dr. Joseph Van Ruymbeke, the inventor of the Van Ruymbeke process of recovering glycerol from soap-lyes, for the first idea of the total acid equivalent and permanent specific gravity determinations.

THE COLUMBIAN UNIVERSITY,  
December 17, 1894.

### ESTIMATION OF TELLURIUM IN COPPER BULLION.<sup>1</sup>

BY CABELL WHITEHEAD.

Received January 2, 1895.

**D**ISSOLVE from twenty-five to fifty grams of the bullion in nitric acid 32° B. and boil off the excess of acid. Add to this solution an amount of a ferric nitrate solution equivalent to 250 mgms. of metallic iron. Precipitate, while hot, with an excess of ammonia, filter, and wash with dilute ammonia until the copper salts are entirely removed, redissolving and reprecipitating if necessary. The residue on the filter contains the tellurium and selenium present in the bullion as ferric tellurites and selenites. This is dissolved in hydrochloric acid, and excess of tartaric acid added, the solution made alkaline with potassium hydroxide, and hydrogen sulphide passed through it, when the tellurium and selenium pass into solution as soluble sulphides. Filter; decompose the alkaline sulphides in the filtrate with dilute hydrochloric acid; allow the liquid to stand in a warm place until the hydrogen sulphide has been removed. Filter again; dissolve the tellurium and selenium sulphides in aqua regia; evaporate the solution to dryness, take up with hydrochloric acid and precipitate the tellurium and selenium from the solution by passing sulphur dioxide through to saturation. Cover the beaker and allow the solution to stand for twelve hours in a warm place, when the precipitate, which consists of tellurium and selenium, is filtered on a tared filter, dried at 100°, and weighed together.

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.

The selenium is separated from the tellurium by boiling the precipitate in concentrated potassium cyanide solution, filtering, and adding hydrochloric acid, when the selenium comes down as a black-red precipitate, which is weighed as before, after drying at  $100^{\circ}$ .

The tellurium is determined by difference or the small amount dissolved by the cyanide solution may be precipitated, after removal of selenium, by saturating with sulphur dioxide, collecting the precipitate with the original residue, and weighing after drying at  $100^{\circ}$ .

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

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### THE USE OF SULPHUROUS ACID ( $\text{HNaSO}_3$ ) IN MANUFACTURE OF GLUCOSE SYRUP AND GRAPE-SUGAR.

BY HORACE E. HORTON.

Received January 18, 1895.

UP to the year 1893 a large quantity of the glucose syrup and grape-sugar offered in home markets was manufactured by a carefully worked-out process, in which sulphurous acid had but little if any place.

While a fine grade of glucose can be manufactured without the use of sulphurous acid, its irrational use has taken full possession of some manufacturers.

That sulphurous acid has a legitimate place in a rational process of manufacture few who have studied the subject will deny, but a great deal of careful work is yet necessary to define the use of this reagent.

I have studied the action of sodium bisulphite on glucose syrup and grape-sugar in several directions, and with interesting results. The bisulphite used was manufactured by Gelian and Co., of New York, who have an excellent article of  $38^{\circ}$ - $40^{\circ}$  Bé. density.

*Preserving Color of Glucose Syrups.*—Numerous experiments have convinced me that sulphurous acid is of great value in preserving the color of glucose syrups. I will present here one

experiment, from the many made, to demonstrate this action of the acid.

On June 21st, fifteen batches (ca. fifty barrels each) glucose syrup were manufactured. Batches 2-9 received one gallon 38° Bé. sodium bisulphite and eight fluidounces of muriatic acid; batches 10-15 received two gallons bisulphite and sixteen fluidounces of muriatic acid.

On July 7th, batches 2-9 had lost color and brilliancy. Batches 10-15 of good color and brilliant.

In September batches 2-9 had a *decided* brown color and had lost brilliancy through separation of gypsum (?). Batches 10-15 good color but not brilliant.

In January, batches 2-9 had a *dirty brown* color. Batches 10-15 a *light* straw coloration.

The bisulphite may be added all to the finished product in the cooler, or a part to the liquor in the 39° Bé. vacuum pan, and the remainder to the finished product in the cooler.

The effect of its addition to the 39° Bé. liquor is immediately perceptible in the bleaching of the light straw-colored liquor.

*Giving Brilliancy to Candy.*—The candy test is for brilliancy and color, and while in some hands gives meaningless results, in skilled hands is a valuable criterion.

This test is carried out as follows: The glucose is weighed into a shallow copper dish along with cane-sugar ("Havemeyer and Elder S. R. Co. 'A' Sugar"), and 150 cc. water added. The proportions of glucose and cane-sugar are the following: For

42°	Bé.	syrup,	8 oz.	glucose	and	1 lb.	9 oz.	cane-sugar;
43°	"	"	8 "	"	"	1 "	10 "	"
44°	"	"	8 "	"	"	1 "	11 "	"
45°	"	"	8 "	"	"	1 "	12 "	"

The dish is placed over the direct flame of an eight-inch Fletcher burner and when the mixture begins to boil, five drops of olive-oil are added to prevent trouble from bubbles. Continue boiling for six minutes, watching carefully the rise of temperature with an accurate thermometer, and when 308° F. is reached, which usually requires nine minutes, pour the hot mass on an

oiled marble slab, when it spreads over the surface, making an irregular circular mass of about fourteen inches diameter.

When the mass has cooled sufficiently *to cut*, divide into halves. Mold one-half into a slab one inch thick, five to six inches long, three inches wide, and wrap in an oiled paper.

The other half is to be cut into strips one to one and a half inches wide, and *without any manipulating*, folded over four times, forming a coil.

From the slab and coil the brilliancy and color are judged. Using a confectioner's glucose made by oxalic acid and run over a dull specially prepared bone-black, a standard candy was prepared having the necessary brilliancy and color.

A large number of glucose samples from sharp bone-black, dull bone-black, specially prepared phosphate bone-black with bisulphite and without bisulphite were made into candy, and in every instance the addition of bisulphite added brilliancy and color.

In connection with candy I must speak of the bugbear sticky candy; there is a great hue and cry attributing sticky candy to the use of bisulphite. I am unable to trace the origin of this assertion to any person, but all are confident of its truth. It may have originated in the practice of preparing syrup for gum-drop manufacturers by adding two and a half buckets of bisulphite and one and a half quarts of muriatic acid to a batch of forty-four barrels 42° Bé. glucose, thus producing an acidity of 0.05-0.055 gram hydrochloric acid in 100 grams syrup. The reasoning may be. If sticky, moist gum-drops are produced by syrup receiving a large quantity of bisulphite, then stickiness and moistness in *all* candy must be due to the use of bisulphite!

I have studied this subject carefully and have been unable to trace sticky candy to the use of bisulphite.

Six samples of candy were boiled using 43° Bé., confectioners' glucose containing two gallons of bisulphite to fifty barrels; six samples of candy using glucose containing eight gallons of bisulphite to fifty barrels.

Three of the candies made from glucose containing two gallons, and three from that containing eight gallons, were exposed

on the laboratory table. Six samples were placed in a closely covered desiccator over sulphuric acid.

It was observed that the samples exposed on the laboratory table grew equally sticky; the samples in desiccator showed no sign of stickiness. This pointed to a certain degree of humidity of the air influencing the stickiness of candy. With this in mind a long series of careful observations were made with reference to the relative humidity of the air, and with the result that stickiness cannot be attributed to the use of bisulphite.

It is interesting to note here, that one candy manufacturer will complain of glucose giving sticky candy, while another manufacturer using glucose from the same batch makes no complaint.

Again, for some unknown reason, it is supposed that glucose receiving over three gallons of bisulphite per batch cannot be used by candy manufacturers for sundry *unknown reasons*! To obtain data bearing on this, batches of glucose were prepared containing five, six, seven, and eight gallons of bisulphite and placed in the hands of a skilled candy manufacturer who knew nothing of the content of bisulphite. In every instance, glucose containing eight gallons of bisulphite gave the best results!

*Influence of Bisulphite on Boiling-Point of Candy.*—The use of a large quantity of bisulphite makes it possible to boil candy to a higher temperature than when no bisulphite or a small quantity is used.

Batches of confectioners' glucose, 43° Bé. density, were prepared from a sharp bone-black and received varying quantities of bisulphite. Candies were boiled and with the following results:

Batch receiving 2 gals. HNaSO <sub>3</sub> boiled to 308° F. Candy good color.					
"	"	2	"	"	" 330° " " very bad color.
"	"	6	"	"	" 308° " " very good color.
"	"	6	"	"	" 330° " Color better, but bad.
"	"	8	"	"	" 308° " Very good color.
"	"	8	"	"	" 330° " Color improv'g but bad.
"	"	10	"	"	" 308° " Very good color.
"	"	10	"	"	" 330° " Color still better.
"	"	12	"	"	" 308° " Very good color.
"	"	12	"	"	" 330° " Good color.



In the manufacture of hydrated grape-sugar having the average composition,

Red substance .....	70.00	per cent.
Water.....	20.00	"
Ash.....	0.52	"
Rest of dextrine.....	....	"
Nitrogenous bodies, etc.	9.48	"
		<hr/>
		100.00
		<hr/>

it will be found that liquor from the second filtration can be treated with sulphurous acid to good advantage; and this accomplished by burning sulphur in a small iron furnace and pumping the fumes into the liquor.

Working with an amount of liquor representing 24,000 pounds finished product, the acidity when

$\frac{1}{2}$ lbs. sulphur is burned, is 0.016 gram HCl in 100 grams.									
1 $\frac{1}{2}$ " " " " " 0.027 " " " " "									
2 " " " " " 0.034 " " " " "									

The use of bisulphite with glucose syrup made it easy to ask the question, What effect will bisulphite have on grape-sugar solutions? Tradition has it that an acidity of over 0.034 gram hydrochloric acid is not allowable; why, no one knows. Some claim that an acidity over this point interferes with the action of the yeast in brewing.

I have experimented in this direction and with the following result:

To batches of grape-sugar sulphured by burning one and a half to two pounds of sulphur and two gallons of bisulphite were added. Laboratory experiments failed to show a diminished activity of the yeast; and more convincing, the brewers using the sugar made no complaint.

It is reasonable to suppose that the slight acidity of 0.034-0.045 gram hydrochloric acid will be taken care of by the calcium carbonate present in water used for brewing.

The addition of bisulphite to grape-sugar solutions led to the interesting observation that crystallization is thereby accelerated. I have made long series of observations and the records clearly show this fact.

I will present a few observations on the subject :

No. of experiment.	Date of manufacture.	Date of observation.	Condition of sample with $\text{HNaSO}_3$ .	Condition of sample without $\text{HNaSO}_3$ .
1.	9.12	9.20	Hardened	Liquor on top
2.	9.11	9.20	"	"
3.	9.19	9.20	Heavy cloud of crystals	No cloud
		9.23	Solid	"
4.	9.23	10.4	"	Little syrup
5.	9.23	10.4	"	Considerable syrup
6.	9.23	10.4	"	Little syrup
7.	9.22	10.4	Little syrup	Great deal of syrup
8.	9.22	10.4	Solid	Little syrup
9.	9.22	10.4	"	Moist
10.	9.22	10.4	"	Very little syrup
11.	9.22	10.4	Plenty syrup	$\frac{1}{2}$ syrup
12.	9.21	10.4	Solid	$\frac{1}{2}$ "
13.	9.21	10.4	"	Mushy
14.	9.21	10.4	"	Little syrup
15.	9.21	10.4	"	$\frac{1}{2}$ syrup
16.	6.21	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
17.	9.20	10.4	Very little syrup	$\frac{1}{2}$ "
18.	9.20	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
19.	9.20	10.4	Solid	$\frac{1}{2}$ "
20.	9.20	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
21.	9.20	10.4	Little syrup	$\frac{1}{2}$ "
22.	9.19	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
23.	9.19	10.4	Solid	$\frac{1}{2}$ "
24.	9.19	10.4	Solid and dry	$\frac{1}{2}$ "
25.	9.19	10.4	$\frac{1}{2}$ solid	$\frac{1}{2}$ "
26.	9.19	10.4	$\frac{1}{2}$ solid	$\frac{1}{2}$ "

The bisulphite bleaches grape-sugar solutions readily, and its effect on the sugar at the end of fourteen days and after six months is very marked.

Added to the "washer batch" (the batch first dropped from vacuum pan after boiling out with muriatic acid) the effect is pronounced.

TOPEKA, KAN., January 8, 1895.

## THE FURFUROL-YIELDING CONSTITUENTS OF PLANTS.

By C. F. CROSS, E. J. BEVAN, AND C. BEADLE.

Received February 13, 1894.

THE chemistry of the formation of the permanent tissue of plants may be approached from various points of view. From the incidents of our working connection with the subject

of cellulose we have, from time to time, dealt with the anterior problem of its elaboration from the point of view of the hexosan complexes which are grouped under this term. De Chalmot, Stone, and others who have followed the pioneering work of Tollens, have been more especially confronted with the relation of the pentoses to plant structure and their life history, and have contributed a very valuable series of investigations now resulting in convincing proofs of important points hitherto of doubtful interpretation.

In the convergence of these two lines of investigation an issue has arisen, and a fundamental problem has become a subject of controversy chiefly between de Chalmot and ourselves.

We have maintained the position:

(1) That the furfurol-yielding constituents of plant tissues are not to be regarded as necessarily and exclusively pentoses or pentosans, since there are oxyderivatives of the hexoses, themselves also C<sub>6</sub> compounds, characterized by the same reactions.

(2) That having regard to the chemistry and physiology of assimilation and cell-respiration in plants, it was probable that the celluloses common with other hexosans would be modified by oxidations of various kinds, these oxidations being probably attended by further combination of the products of oxidation with the parent complex, *i. e.*, with the unchanged residues of the complex.

(3) That, therefore, we may expect to find in the celluloses, furfurol-yielding groups, *not* pentoses.

Upon the subsidiary question as to whether the actual formation of furfurol is not always preceded by a change to a pentose configuration with elimination of the fully oxidized C. position, we expressed no opinion. It is, in fact, altogether irrelevant to the point at issue, which is simply that of the molecules as occurring in the plant tissue.

The controversy has proceeded by stages in the following publications, which we cite in order of time.<sup>1</sup>

The purpose of this communication is to point out, as briefly

<sup>1</sup> Cross, Bevan, and Beadle, *Ber d. chem. Ges.*, 26, 3520; 27, 1061; De Chalmot, 27, 1489, 2722.

as possible, that de Chalmot, in his latest communication,<sup>1</sup> closes the controversy in a manner satisfactory to ourselves, although appearing still to join issue with us. It is very necessary to quote two paragraphs from the paper:

(1) p. 589. "*Are there pentosans in plants which are formed from seeds which germinate in darkness?* It has become necessary to answer this question since Cross, Bevan, and Beadle, in a recent article, assert that the furfural-yielding compounds in the sprouts, which are developed from barley in darkness, are so-called oxycelluloses and are not pentosans."

(2) p. 610. "I wish now to put forward the following hypothesis: Pentose molecules are formed in complex molecules of hexosans (celluloses and hemi-celluloses), in which a part or all of the aldehyde groups have been bound by condensation and are thereby preserved from further oxidation."

This is precisely all that we have contended for. The second paragraph is the answer, from our point of view, to the question contained in the first.

We are dealing, in fact, with an oxycellulose series and the only remaining point at issue between us is this: We are of the opinion that the series is represented in the living tissues. De Chalmot holds that the pentoses are, as it were, explosively formed; the fully oxidized C. group preferring rather a summary exit than the alternative of combining with the basic or alcoholic groups of unaltered hexose or hexosan molecules. This view is, we think, at variance with the perspective of metabolism generally, and certainly contrary to what we know of the chemistry of the oxycelluloses, their very gradual formation under oxidizing treatment, and the intimate union contracted between the oxidized groups and unaltered molecules of the parent cellulose.

Since the final solution of the problem of the constitution of these "natural oxycelluloses" must take the form of quantitative resolution into molecules of simpler, if not the simplest form, it need not be further discussed *a priori*.

We are engaged in a study of their systematic dissection and the results will be communicated in due course.

<sup>1</sup> Am. Chem. J., 16, 589-611.

Of course, it will be understood that these criticisms in no sense lessen the value of the contributions of de Chalmot, and his fellow specialists in the subject of the pentosans, to the general problems of assimilation and metabolism. Any error which may have been made is one only of interpretation. The too free use of "pentose" and "pentosan" as the equivalent of "furfural-yielding constituents" will prove, we think, to have temporarily obscured some important points in the physiology of the elaboration of plant tissues, but there being now a substantial agreement in the main issue it may well be left to time and experimental investigations to "materialize" this further chapter in the life of the plant cell.

4 NEW COURT, LONDON, W. C.,  
January 30, 1895.

## THE SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

BY E. TWITCHELL.

Received January 25, 1895.

THE fatty acids insoluble in water, which constitute the greater part of most natural fats, are probably always found as a mixture of two groups, one composed of saturated, the other of unsaturated compounds, the former belonging to the acetic series and the latter to the acrylic and other series containing still less hydrogen. In most fats of commercial importance, such as tallow, lard, cottonseed-oil, and some other vegetable oils, the first named group is represented by only two members, stearic and palmitic acids, which are solid at ordinary temperatures, while the last contains the liquid oleic and linolic acids.

An accurate separation of these groups ought to be the first step in the analysis of any fat, as without it other quantitative reactions, such as the amount of iodine absorbed or alkali combined by the fatty acids, would lead to no very definite conclusions regarding the actual composition of the mixture.

Although a number of analytical methods have been proposed to obtain this separation, their accuracy has not been without question, while in my work I have, at different times, attempted to separate solid from liquid fatty acids and entirely failed to obtain satisfactory results. It therefore seemed to me very

desirable to make a study of some of the methods which have been published, together with any modifications which might suggest themselves in the course of the work. In the following experiments it was attempted not only to compare the different methods, but to determine, if possible, by some direct test, the degree of accuracy of each.

Varrentrapp observed that the lead soap of the solid and liquid fatty acids show great difference in respect to their solubility in ether, soaps of the liquid acids being readily soluble, while those of the solid acids are almost, if not quite, insoluble. On this property of lead soaps have been based the methods which seem to promise the best results, though other solvents than ether have been recommended.

1. Perhaps the most carefully worked-out process is that of Muter, described in the *Analyst* of April, 1889, which has been employed in examining lard chiefly for the purpose of detecting an adulteration of cottonseed-oil or stearine. This method has been examined and slightly modified by Nathaniel J. Lane, who has published his results in this JOURNAL, February, 1893. According to this process, the neutral potassium soaps of the fatty acids in boiling water are precipitated by lead acetate. The lead soaps which adhere to the sides of the vessel are washed several times with boiling water, dried as quickly as possible, and then boiled with redistilled ether and allowed to cool thoroughly, filtered, washed, and the filtrate, containing the lead soaps of liquid acids, decomposed with hydrochloric acid and water. The ethereal solution of fatty acids floats on the acid liquid. An aliquot part of this solution is titrated with standard sodium hydroxide to determine the percentage of liquid acids, and another part is evaporated and dried in a current of carbon dioxide and treated with Hübl's solution. Muter finds about ninety-four per cent. as the amount of iodine absorbed by the liquid acids of lard.

Having carefully prepared the insoluble fatty acids of lard rendered in my laboratory (saponifying in the usual manner and decomposing with hydrochloric acid while avoiding exposure to air as much as possible), I carried out the process of Muter, following carefully all important details. A part of the ethereal

solution of liquid fatty acids obtained was put into a weighed Erlenmeyer flask provided with a ground-glass stopper; then dried on the water-bath in a strong stream of carbon dioxide, which had been washed by passing through sodium bicarbonate solution and dried over calcium chloride. After thoroughly cooling the flask, dry air was drawn through for a few minutes to remove carbon dioxide, and the flask weighed. The percentage of iodine absorbed by these fatty acids was then determined in the usual manner, the operation being conducted in the same flask. The object in finding the iodine absorption was to determine, at least comparatively, the purity of the liquid fatty acids, *i. e.*, their freedom from saturated compounds. The following iodine numbers were found:

	Iodine absorbed. Per cent.
Lard . . . . .	56.27
Fatty acids of lard . . . . .	{ 58.49 59.26
Liquid acid by above process . . . . .	94.06

In order to test the solubility of lead stearate and palmitate in ether, a mixture of stearic and palmitic acids, such as is found in commercial stearic acid, was purified by crystallization from alcohol till it gave an iodine number equal to zero. The lead soap was then prepared by the above-described method and a small quantity boiled twice with alcohol to remove free fatty acids and then treated with boiling ether and allowed to cool. At 25° C. 100 cc. of ether dissolve 0.015 gram of the lead soap, and this does not crystallize out at 0° C. This would cause an error of about one per cent. in the above process, while it is possible that, in the presence of lead oleate the solubility of the stearate and palmitate might be much greater.

Another and more serious objection to Muter's method consists in the unavoidable exposure of the lead soaps to the air. All my results seem to show that the lead soaps of the unsaturated fatty acids oxidize even more readily than the free acids. So that, though great care is taken to remove the liquid acids from the air, it does not seem possible to treat lead soaps in this way without a good deal of oxidation, especially during the tedious filtration. Fahrion has noticed this remarkably rapid

oxidation in the case of calcium soaps (*Chem. Ztg.*, 1893, 17).

2. In his book, *Chimie Analytique des Matières Grasses*, Jean describes a method of examining lard. This method—modified in the manner of treating the liquid acids—was next employed. Four grams of the same lard fatty acids were dissolved in fifty cc. of ninety-five per cent. alcohol; and to this was added two and a half grams of lead acetate dissolved in twenty cc. of the same alcohol, both solutions being hot. There was an immediate precipitate, and the mixture was allowed to stand one hour at the temperature of the laboratory, and then cooled to 15° C. and kept at this temperature one hour longer. A part was then filtered into a separatory-funnel, treated with ether and dilute hydrochloric acid, washed, and dried in carbon dioxide. The iodine number of these liquid fatty acids was found as in the previous experiment, and their percentage in the original solution calculated. The precipitate was washed thoroughly with ninety-five per cent. alcohol, decomposed with hydrochloric acid, and the solid fatty acids separated and weighed. Their iodine number was also obtained. The following were the results:

	Per cent. obtained.	Iodine absorbed. Per cent.
Solid fatty acids .....	46.24	4.90
Liquid fatty acids.....	51.82	103.37

These figures indicate a fractional precipitation in which all the solid and a part of the liquid acids are precipitated. The iodine number of the solid acids and the low yield of liquid acids both point to this. That part of the liquid acids in the solution is probably held there by the acetic acid liberated. This must be the case as lead oleate is only slightly soluble even in absolute alcohol.

If the liquid acids, precipitated along with the solid, consisted entirely of oleic acid as was probable, the iodine number of the liquid part of the fatty acids would be somewhat lower than 103.37 per cent. Yet the amount of liquid acids precipitated being in this case quite small, could only reduce the result by two per cent. at the most. The great difference between this iodine number and that of the liquid acids obtained by Muter's method show that the latter must have contained a considerable amount either of saturated or of oxidized fatty acids.



Jean gives the iodine number of the liquid acids of lard as 92.71. This low figure may be accounted for by the fact that he does not take the precaution to dry the fatty acids in a current of carbon dioxide.

3. It appeared desirable to determine first, whether the liquid acids obtained by the last process were entirely free from solid acids, and second, whether the precipitation was actually a fractional one, more or less of the liquid acids precipitating according to circumstances of temperature, concentration, etc. In order to decide these questions, four grams of lard fatty acids (prepared at another time and from another sample of lard) were dissolved in ninety-five per cent. alcohol and precipitated with lead acetate, cooled for one hour to  $15^{\circ}\text{C}$ ., and filtered. Ten cc. of the filtrate were drawn off, decomposed with hydrochloric acid, the fatty acids dried in carbon dioxide, and treated with Hübl's solution as before, while the remainder of the filtrate was cooled for one hour to  $0^{\circ}\text{C}$ . At this temperature there was an additional precipitate. This precipitate was filtered off and washed with ninety-five per cent. alcohol, the washings being thrown away. The fatty acids obtained from the filtrate were also treated with Hübl's solution. The iodine absorbed by the fatty acids of these fractions was as follows:

	Amount obtained.	Iodine number.
Lard fatty acids		62.57
Fatty acids from filtrate at $15^{\circ}$	0.2675 gram (46.81%)	109.35 per cent.
" " " precipitate at $0^{\circ}$	0.1020 "	
" " " filtrate at $0^{\circ}$	0.1915 "	118.02 per cent.

The fatty acids obtained from the precipitate at  $0^{\circ}$  chilled at  $0^{\circ}\text{C}$ . and melted at  $7^{\circ}\text{C}$ . It could therefore contain little or no solid acid, and was probably pure oleic acid. Its iodine number was not determined, but calculating from the iodine number of the filtrate at  $0^{\circ}$ , it must be very nearly 90—that of oleic acid—to make the iodine number of the mixture 109.35.

It is plain from the above results that the precipitation of fatty acids by lead acetate in alcohol is not a quantitative separation but a fractional precipitation, in which the solid acids are precipitated first, then oleic acid, and finally linolic acid.

Though no quantitative separation of the liquid acids has been

made, their percentage can be calculated as follows: The percentage of liquid acids in the alcoholic filtrate is calculated from the fraction drawn off. This is multiplied by the iodine number of these fatty acids. The result is deducted from the iodine number of the original fatty acids. The difference represents oleic acid. Dividing this by 0.9 gives the percentage of oleic acid precipitated with the solid acids. Adding this to the liquid acid in the filtrate gives the total liquid acid. In the case of the last sample the calculation is: 46.81 per cent.  $\times$  109.35 per cent. = 51.19. Deducting from 62.57 gives 11.38. Divide by 0.9 = 12.64, oleic acid in precipitate; add to 46.81 gives 59.45, total liquid acids; whose iodine number is  $\frac{62.57}{59.45} = 105.2$ .

The linolic acid is easily calculated from the iodine absorption of the liquid acids—109.35 represents 78.5 per cent. oleic acid, 21.5 linolic acid.  $21.5 \times 46.81 = 10.06$  per cent. linolic acid in the original fatty acids.

4. A process described by R6se (*Repert. f. analyt. Chem.*, 1886) consists in shaking the ethereal solution of fatty acids with finely powdered litharge, when the lead soaps are formed and those of the liquid acids remain in solution. This method was next employed, using not ether, however, but petroleum ether, completely volatile at 80° C., in which I had found lead stearate and palmitate to be much less soluble than in ether. 100 cc. of petroleum ether at 30° C. was found to dissolve 0.0034 gram of the mixed soaps while at 5° only 0.0018 gram were dissolved. Two and a half grams of the lard fatty acids used in the last experiment were dissolved in fifty cc. of petroleum ether, two and a half grams of lead monoxide added, and allowed to stand two hours in a warm place with frequent agitation. A fifty cc. flask was used having a graduated neck. It was filled almost to the stopper in order to avoid the oxidizing effect of the enclosed air. After two hours time the yellow lead monoxide had become white in appearance, due to the formation of lead stearate and palmitate, and the precipitation was judged to be complete. It is clearly not necessary to combine the lead with all the fatty acid. If a part of the liquid acids are in the form of lead soaps this will be a guarantee that all the solid acids have combined. The presence of lead in the filtrate will show

whether the agitation has been continued long enough. Before filtering, the flask was placed in ice-water for half an hour in order to insure as complete a precipitation as possible. Then it was filtered, a definite part of the original volume pipetted off, decomposed with hydrochloric acid in a separatory-funnel, and evaporated and dried in a current of carbon dioxide as before. The liquid acids calculated to the whole solution yielded 55.10 per cent. having an iodine number of 108.66. The precipitate on washing then decomposing with hydrochloric acid gave 44.70 per cent. solid acids having an iodine number of 3.02 per cent. This impurity was probably caused by an oxidation of the liquid acids to compounds whose lead soaps were insoluble in petroleum ether.

The results obtained here are not far from those calculated by the alcohol method. The petroleum ether method would have the advantage over the other in that the iodine number would be that of the liquid acids and not only of a fraction from which part of the oleic acid has been precipitated. On the other hand a quantitative result by the petroleum ether method could only be arrived at where the fat is perfectly fresh and the greatest precautions have been taken to avoid oxidation during the whole manipulation. The same sample of lard fatty acids, after standing seven days in a closed jar, gave the following results :

	Iodine number.
Solid acids.....	10.1 per cent.
Liquid " .....	101.7 "

The oxidation had given products both soluble and insoluble in petroleum ether ; and in this case the percentage of liquid acids cannot be inferred from the analysis.

A precipitation of all the solid and part of the liquid acids by lead acetate in alcohol, by the method described by Jean, with the addition I have proposed of finding the iodine number of both the original fatty acids and those in the solution, and calculating therefrom, would give accurately the percentage of solid and liquid acids in a fat. Such a method would perhaps be too cumbersome for general commercial work. Still I believe it is at present the only positive solution of the problem.

## IMPROVED METHODS OF WATER ANALYSIS.

BY IRVING A. BACHMAN.

Received January 2, 1895.

WE have in the South Atlantic States incontestable evidence that the true source of malarial disturbance is to be found in the water, and not in the air, as was formerly supposed. The introduction of deep-seated artesian wells has very materially decreased this trouble, and has rendered localities that were notoriously unhealthy, perfectly healthy.

The examination into the exact difference between the malaria-producing waters and those proof against it, has had the writer's attention for over two years, and the work herein detailed is a portion of the preliminary work looking into the best methods of analysis.

My experience with the Wanklyn process as ordinarily carried out with the usual apparatus, so impressed me with its crudeness, that for a long time I have had little confidence in the results I obtained. The loss by imperfect condensation, the crude way of adding the permanganate solutions, and the open-air contamination of the distillate are by no means in keeping with accurate work. The loss by imperfect condensation is very much greater than we permit ourselves to believe, and with the original Wanklyn process<sup>1</sup> is a very difficult matter to control; the loss is variable, and is dependent upon the rate of distillation and the efficiency of the cooling apparatus. After making a long series of experiments upon every character of material liable to be found in water, I am satisfied that a rate exceeding fifty cc. in fifteen minutes is accompanied by loss. As a modification of the Wanklyn process, Mallet<sup>2</sup> proposes to keep the original volume of liquid in the retort constant by the systematic addition of ammonia-free, distilled water, in order to prolong the action of the permanganate; this is objectionable, inasmuch as the operation is endangered by a constant source of error in the addition of ammonia-free water, which is difficult to obtain in so large a quantity.

<sup>1</sup> Wanklyn and Chapman Water Analysis, (6th ed.), 1884, pp. 38-40.

<sup>2</sup> Report National Board of Health, 1882, p. 210.

In my own work I had frequently noticed that the evolution of ammonia very often increased as the liquid in the retort became more concentrated.

Acting on this observation it occurred to me that by the action on a smaller and limited quantity of water by the full strength of the permanganate solution and supplying the water under examination at about the rate of distillation, very much better results could be obtained ; this I have now confirmed by a great many comparative analyses.

The apparatus used is shown in Fig. 1, and consists of distillation flask A, of one liter capacity, into which is fitted by a ground joint the remainder of the apparatus (this is the only

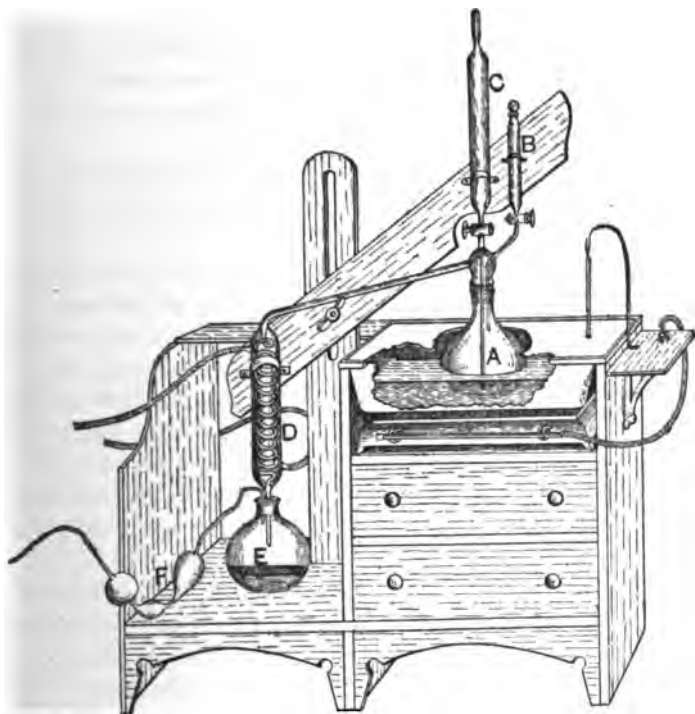


FIG. 1.

connection the apparatus has) ; through the bulb of the neck we have two burettes with stop-cocks, the smaller, B, with a capacity of fifty cc., with its tube projecting within three inches

of the bottom of the distillation flask ; the larger burette C, has a capacity of 250 cc. and its tube projects to within one-half inch of the bottom. The cooling apparatus D, is a closely coiled glass worm, with a long projection at the lower extremity, to which is attached the distillate vessel E, by a soft rubber stopper, which also has tube for connection with the Will and Varrentrapp absorption bulb.

The apparatus is constructed to work under greatly reduced pressure, and the connection with distillation flask, as well as the stop-cocks, are accurately ground to remain tight without a lubricant.

The apparatus is mounted as shown, raised and lowered into the bath by means of a thumb-screw, as indicated. The whole is very easily managed, and is very serviceable. I have made over a thousand determinations with mine, and there is no reason why it will not continue to do good service for a very long time to come.

The heating of the apparatus is effected by setting the flask into a fixed saline-bath, with a covered top as shown, and heated from below by a two-pipe gas-burner.

*Mode of Procedure.*—After thoroughly rinsing the apparatus with ammonia-free distilled water, 500 cc. of the water under examination are put into the flask and the apparatus connected and lowered into the bath, the distillate flask with Will and Varrentrapp bulb, the latter previously charged with Nessler solution, are now attached and connected with the pump.<sup>1</sup> The partial vacuum is now established gradually, the sodium carbonate solution added by way of the smaller burette, and the distillation started and continued until 200 cc. have been distilled over, which is then nesslerized for free ammonia.

The vacuum tube is now disengaged and the stop-cock on large burette opened and about 250 cc. of the liquid in the distillation flask drawn up and the fifty cc. of alkaline permanganate solution, previously poured into the smaller tube, is now allowed to run in after the distillate flask has again been attached.

<sup>1</sup> Richards is an excellent device, but it is important to have a small check-valve in the tube to prevent the water being drawn into the apparatus when the water pressure is suddenly diminished. A very simple valve is made of oiled silk opening only toward the pump.

We now have fifty cc. of alkaline permanganate acting on fifty cc. of water, and after, say thirty to forty cc. have been distilled over, the water in the large tube is allowed to drop in at the same rate as the distillation, which must not exceed fifty cc. in fifteen minutes. [The rate of distillation, as recommended by the Chemical Section of the American Association for the Advancement of Science, *i. e.*, fifty cc. in ten minutes, is too rapid, and is very frequently accompanied by loss by imperfect condensation; this is very readily observed in my apparatus by discoloration of the Nessler solution in bulb.] The distillation is continued until 250 to 300 cc. have been distilled over, which is then nesslerized.

The following notes from my laboratory work will show the general plan of the work :

One gram urea was *dissolved in one liter* ammonia-free water.

1. Ten mgms. urea in 300 cc. of ammonia-free water, 250 cc. drawn up into tube, fifty cc. permanganate solution added, bath  $87^{\circ}\text{C}$ ., cooling water  $28^{\circ}\text{C}$ ., pressure six and a half inches, distillation at rate of 150 cc. per hour, 310 cc. distilled over with slight discoloration of Nessler bulb.  $30.2 : 2.0 :: 310 : 2.053$  mgms. ammonia, or 20.53 per cent. which is 36.2 per cent. on ammonia obtainable.

2. Five mgms. urea in 300 cc. ammonia-free water treated as above—297.4 cc. distilled over, no discoloration of Nessler bulb.  $28.8 : 1.0 :: 297.4 : 1.032$  mgms. ammonia, or 20.64 per cent. which is 36.4 per cent. on ammonia obtainable.

3. Ten mgms. urea in 300 cc. water, 250 drawn up, fifty cc. permanganate solution added, bath  $85^{\circ}\text{C}$ ., cooling water  $27^{\circ}\text{C}$ ., pressure five inches, rate of distillation, 100 cc. per hour, 290 cc. distilled over, no discoloration of Nessler bulb.

$25.1 : 2.0 :: 290.0 : 2.310$  mgms. ammonia, or 23.10 per cent. on 40.7 per cent. on ammonia obtainable.

4. Ten mgms. urea in 500 cc. water, ten cc. strong solution sodium carbonate added, bath  $87^{\circ}\text{C}$ ., cooling water  $28^{\circ}\text{C}$ ., pressure five and a half inches.

210 cc. distilled over as free ammonia, which yielded 0.835 mgms. ammonia or 8.35 per cent.

250 cc. were then drawn up, fifty cc. permanganate solution added, and distilled as before.

305 cc. were distilled over, which yielded 2.296 mgms. ammonia, or 22.96 per cent.

Total ammonia 8.35 per cent. free, plus 22.96 per cent. albuminoid, or 31.31 per cent. which is 55.2 per cent. on ammonia obtainable.

Rosaniline hydrochlorate yielded 86.02 per cent. on ammonia obtainable.

Strychnine sulphate	"	78.10	"	"	"	"
Urea-boiling five hours	"	79.90	"	"	"	"
Cyanuric acid	"	61.10	"	"	"	"
Quinine sulphate	"	77.09	"	"	"	"
Morphine sulphate	"	81.11	"	"	"	"

The apparatus, Fig. 1, is also used for the Kjeldahl process. This process was first described for use in general water analysis by Drown and Martin,<sup>1</sup> and is now very generally used in place of the Wanklyn process.

I have modified the Kjeldahl process so as to insure more perfect decomposition, and have obtained most gratifying results with the most obstinate organic compounds.

*Process.*—300 cc. of the water under examination is put into the distillation flask of apparatus already described (Fig. 1) and the whole connected up; ten cc. specially prepared concentrated sulphuric acid is allowed to drop in slowly by way of the smaller burette, the whole is then allowed to digest at 85° C., under diminished pressure for, say one hour, and then brought to a boil, and so continued until the contents are colorless. The acid is then neutralized and the solution rendered strongly alkaline by the addition of fifty cc. strong solution of ammonia-free, sodium hydroxide through the smaller tube.

250 cc. of the contents are then drawn up into the larger tube and fifty cc. of permanganate solution added through the smaller tube, and the distillation carried on as already described in the modifications of the Wanklyn process, and nesslerized as before.

The modified process combines the good features of the Wanklyn and Kjeldahl, and is easily carried out with the apparatus described. The original sources of error are now practically eliminated.

The following are some results upon some of the substances

<sup>1</sup> Technology Quarterly, 2, 3.



that with the Wanklyn process yield only a very small percentage of the ammonia. I have made no comparative tests with the original Wanklyn process, and quote Mallet's:<sup>1</sup>

Mine.	Mallett, by Wanklyn's Process.
Rosaniline hydrochlorate 96.9 per cent.	23.8 per cent of theoretical amount.
<sup>2</sup> Cyanuric acid	
(distillation two hours) 89.1	2.1
Cyanuric acid	
(distillation four hours) 91.2	
Urea (from urine)..... 100.3	22.2
Urea (from ammonium	
cyanate)..... 99.0	20.8
Potassium ferrocyanide 59.8	none

In nesslerizing I have found the Leed's Comparator modified as in Fig. 2, best suited to my wants. The work is very much facilitated by having one tube with stop-cock carefully graduated up to 100 cc., and connected to another tube, as shown in Fig. 2 ;



FIG. 2.

by using the blowing tube the liquid can be raised or lowered at will, and compared with the known solution with a nicety and exactness that I have been unable to attain by any other plan.

*Combustion Process.*—The Frankland combustion process<sup>3</sup> is entitled to more general use for regular work on water analysis; in my hands it has yielded satisfactory results after eliminating the objectionable features of open-air evaporation.

<sup>1</sup> Report Board of Health, page 253-254.

<sup>2</sup> After standing over night yielded 1.7 per cent. additional.

<sup>3</sup> Frankland : Water Analysis, London, 1890.

The apparatus designed for this purpose is shown in Fig. 3, and is constructed to hold a vacuum of fifteen mm. for four hours after pump has been stopped. The vessel A is set into a fixed table water-bath, to a depth of two inches, and the water under examination, in closed reservoir, B, the capacity of which is 200 cc., is admitted into A by a tube of very fine bore, and the vapor of water carried over into the sulphuric acid absorption col-

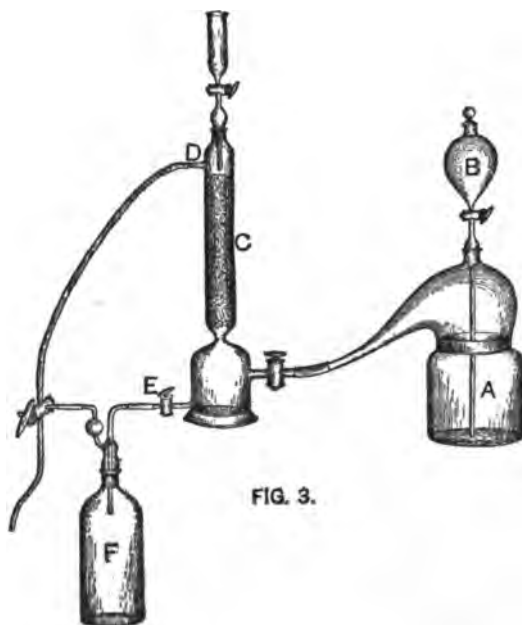


FIG. 3.

umn C, which is filled with broken glass tubing and has traveling through it, pure concentrated sulphuric acid. The vacuum tube to jet-pump is connected to the upper, D, and lower, E, connection of the absorption column by a three-way cock, by which the operation is momentarily suspended and the vacuum held, while the acid accumulated in the lower part of the column is drawn into a bottle, F, by diminished pressure.

Concentrated sulphuric acid is such a powerful absorbent that under the vacuum produced by a good jet-pump, ice can be readily and rapidly formed in the vessel, so that with the water in the bath at  $30^{\circ}\text{C}.$ , the evaporation is rapid; actual boiling,

however, must not be permitted. The water is admitted only at the rate of evaporation which can be adjusted to a nicety by the stop-cock. Care must be taken to start the pump cautiously, thereby establishing the vacuum gradually, and to have only a thin layer of water in the vessel to avoid serious spattering in the escape of the bubbles of gas. In this way 500 cc. of water is evaporated to dryness in six to seven hours, and requires little or no attention after the apparatus is once adjusted.

The following comparative experiments have been made on water:

PARTS PER MILLION.				
	Wanklyn.	Wanklyn with my modifica- tions and apparatus.	Kjeldahl, Drown, and Martin.	Kjeldahl with my modifica- tions and apparatus.
	Free and albuminoid ammonia.		Organic nitrogen cal- culated as ammonia.	
Savannah river at } Augusta.....	Free, 0.011 Albu., 0.130	Free, 0.010 Albu., 0.165	0.172	0.175
	0.141	0.175		
Savannah river, at } 26 feet.....	Free, 0.180 Albu., 0.135	Free, 0.183 Albu., 0.236	0.421	0.420
	0.315	0.419		
Well water, Sum- } merville.....	Free, 0.092 Albu., 0.116	Free, 0.105 Albu., 0.186	0.285	0.287
	0.208	0.291		
Spring water sup- } plying Hotel Bon } Air.....	Free, 0.015 Albu., 0.123	Free, 0.018 Albu., 0.209	0.205	0.219
	0.138	0.227		
Driven well, be- } low Augusta... }	Free, 0.685 Albu., 0.605	Free, 0.700 Albu., 0.976	1.855	1.867
	1.290	1.676		
Driven well in So. } Carolina..... }	Free, 0.416 Albu., 0.395	Free, 0.422 Albu., 0.566	1.116	1.121
	0.811	0.988		
Artesian well } water, Georgia } Chem. Works.. }	Free, 0.005 Albu., 0.036	Free, 0.005 Albu., 0.042	0.050	0.050
	0.041	0.047		
Distilled water } with 10 per cent. } of water from pool } in garbage pile.. }	Free, 0.620 Albu., 1.136	Free, 0.653 Albu., 2.251	3.007	3.100
	1.756	2.904		

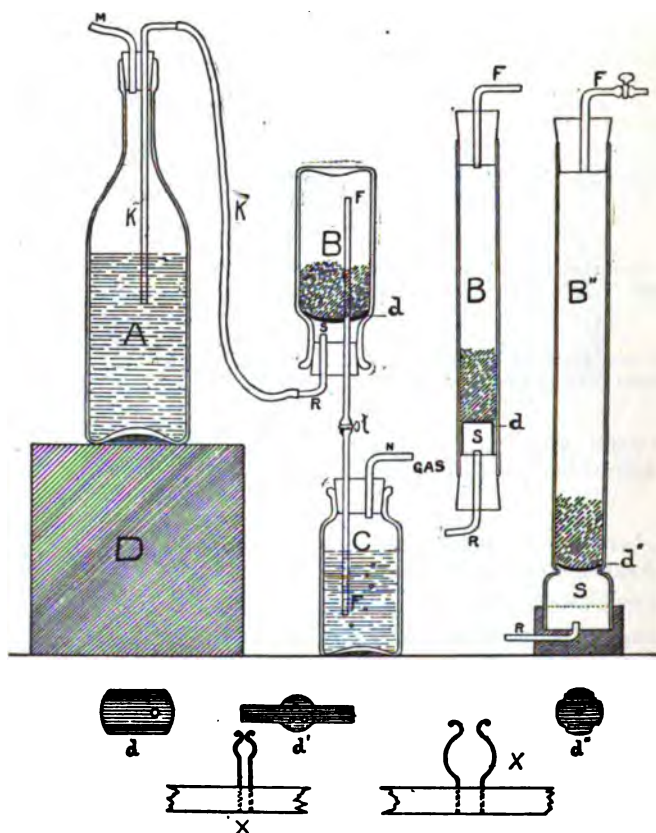
Augusta, Ga., December, 1894.

## A CHEAP FORM OF SELF-REGULATING GAS GENERATOR.

BY W. W. ANDREWS.

Received February 6, 1895.

**T**HIS form of generator is so cheap and easily set up that it makes it possible for every teacher and experimenter in chemistry to have, at practically no expense, a set of generators



capable of yielding, whenever called upon, a supply of hydrogen, hydrogen sulphide, chlorine, carbon dioxide, sulphur dioxide, etc. It consists of an ordinary bottle, A, to serve as reservoir

for the acid, a smaller bottle, B, which is the generator proper, and C, the familiar wash-bottle. A is closed by a cork holding two pieces of glass tubing. The one *m* just pierces the cork and the other, *k*, reaches down a short distance below the surface of the acid and is connected by means of a rubber tube with *r*, thus forming a siphon leading from A to B, as shown in cut. The tube *m* is used to start the siphon *kr* by blowing into A while the stop-cock, *l* is open. *r* is the exit tube for the gas. The charge of solid in B rests on a shelf of sheet lead, *d*, the width of which equals the diameter of the neck of the bottle, and its length the internal diameter of the bottle. It serves the purpose of securing a space, *s*, which prevents the extra gas generated, when *l* is closed, from pressing the acid out of the siphon. Instead of a bottle for holding the charge a calcium chloride tube, or an Argand lamp chimney, with its larger end closed with a cork or sunk into a wooden block and cemented with paraffin wax, or even a piece of large-sized tubing may be used. If the last be used the space *s* is secured by cutting the lead in the shape *d'* and bending it to form a bench to support the solid charge, as shown. *d''* is the shape of the lead support to be used in the calcium chloride tube or Argand chimney. *x* and *x'*, are the wire springs for holding B to its support, from which it may be lifted or replaced instantly. One is to enclasp the body and the other the neck of the bottle, or one of the glass tubes below the cork.

The advantages of this form of generator are:

1. Its cheapness. An ordinary fruit-juice bottle and two wide-mouthed eight-ounce bottles will, with the necessary tubing, make one of good capacity.
2. Its convenience and safety. It is strictly self-regulating. If a rubber tube fitted with a glass plug one-half inch long, instead of a stop-cock be used, the gas flows only when the fingers pinch up the rubber along one side of the plug and ceases the moment they are lifted. The apparatus, therefore, is self-closing. It is very easy to recharge either with acid or solid.
3. It ensures a more even quality of gas than the well-known Kipp, and as complete utilization of the acid as the Koninck generator. When the gas presses the acid back from B, it enters A laden with dissolved solid and, on account of its greater specific gravity,

it falls in a straight line to the bottom, where it spreads out in a dense layer. When the apparatus is again set working, the purest acid is drawn from the upper layers. There is, consequently, some advantage in using a tall bottle for A.

4. It may be put together in a form which has all the advantages possessed by the Schanche generator (see this JOURNAL, Dec. 1894.) Making the glass tube R, long enough to reach to the top of B, and to curve a little downward, so that the acid may drop on the top of the solid charge and trickle through it. A drainage-tube with stop-cock must be inserted into the cork to carry off the used-up acid from the space S. The inverted bottle for B, possesses this advantage over the calcium chloride tube or chimney; *viz.*, that owing to the position of the mouth of the gas exit tube R, solid particles are not so likely to be shot into it when the acid is vigorously attacking the solid charge.

5. The pressure can be regulated at will by placing A at different heights, and this pressure may, at any moment, be reinforced by blowing into A, and the reinforcement held by closing M by means of a rubber tube and pinch-cock.

### SOME OF THE PROPERTIES OF CALCIUM CARBIDE.

BY F. P. VENABLE AND THOMAS CLARKE.

Received February 7, 1895.

THE calcium carbide used was prepared by the Willson Aluminum Company. In this preparation, lime is mixed with some form of carbon, as coal-tar; the mass is then heated, with stirring, until a thorough mixture is obtained. The proportions are so arranged that the mass becomes dry and hard on cooling. This mass, in lumps, is then placed in the electric furnace. In a very short time after the turning on of the current, the process is complete. The molten mass can be run out of the crucible or it may be removed after cooling. On examination, it is easy to see that there is more or less of carbon unchanged, or rather converted into the graphitic variety by the intense heat. Along with this are to be seen crystalline masses, lustrous and dark brownish black in color.

These are quite hard, and break with a crystalline fracture. Several efforts at effecting a separation from the graphitic carbon

were unsuccessful. The luster is slowly lost on exposure to air, more rapidly if the air be filled with moisture. The whole will finally crumble down into a gray powder with particles of black graphite interspersed through it. The carbide can be kept for a year or two if placed in a tightly stoppered bottle and is quite easily preserved if a little coal-oil is placed in the vessel containing it.

By far the most interesting property of this carbide is its decomposition when brought in contact with water. The metallic carbides seem to be distinguished by the ease with which they exchange their carbon for the oxygen of water or for the radicals of various acids, the carbon combining with the hydrogen to form various hydrocarbons. Several authors have reported that the decomposition of this particular hydrocarbon caused the formation of acetylene. Experiments were carried out by us proving this fact, some time before there were any publications concerning it in the chemical journals, but we were not at liberty to publish anything concerning it at that time. If the gas, as evolved, is passed through a set of absorption flasks containing ammoniacal copper solution it will be entirely absorbed, not a bubble passing through, out of one or two liters of the gas. Thus it seems to be pure acetylene. The amount of gas yielded by any one sample will be affected to some extent by the amount of graphitic carbon present. Hence different lots will vary somewhat. The average is about 200 cc. to the gram of carbide.

If the gas be ignited as it is evolved it gives a smoky flame; if it be considerably diluted, as one part of gas to from six to ten of air, a flame of great brilliancy and intensity is gotten. A company has been formed to introduce this as an illuminant upon the market. The cheapness of the materials used and the ease with which the gas can be formed ought to make it a valuable and useful addition to our illuminants. If too large a proportion of air be admixed a very violent explosion can be brought about by igniting it. In some cases we have noticed the flame rapidly travelling backwards along a rubber tube towards the gasometer in which the gas was stored. One explosion taught us that care was necessary in handling the mixture.

Several analyses were attempted of the carbide, but for obvious

reasons failed to give very satisfactory results. In the first place there was uncombined carbon present, also a small portion of a tarry matter which could be detected by heating to high temperatures, and lastly, the specimens worked upon were several months old and in spite of careful keeping, had been slightly acted upon by the air and so contained uncombined lime or calcium carbonate. Moissan gives  $C_2Ca$  as the formula calculated from his analyses. This would agree well with the decomposition by water;  $C_2Ca + H_2O = C_2H_2 + CaO$ .

*Action of Hydrogen upon the Carbide.*—Dry hydrogen has no action upon this carbide in the cold. Several small pieces of the carbide were placed in a piece of combustion tubing, drawn out at one end to a point suitable for testing the flame. Dry hydrogen was then passed over it and as soon as the air was expelled the hydrogen was ignited at the jet and a lamp placed under the tube so as to heat the carbide. In a little while the colorless flame became luminous and remained so a short time. A brownish tarry matter condensed in the cooler parts of the tube. The mass of the carbide assumed a dull gray tint and a very thin white sublimate collected at a short distance from where the tube was heated. The ignition was carried on for five hours. The driving off of this tarry matter seemed to be the only action. The substance on removal from the tube, was still hard. On exposure to the air, it disintegrated, and, if thrown into water, it was decomposed, showing the same behavior as the original carbide.

*Action of Air and of Oxygen.*—Some fresh pieces of the carbide were placed in the tube and heated while dry air was passed over them. A luminous flame was gotten as before and the same tarry matter was driven off and then there seemed to be no further action. Tests showed the carbide apparently unchanged at the end of prolonged heating.

Oxygen was then passed over some of the carbide which was being moderately ignited. No change was observed after two hours' heating. If the temperature was very high, such as that gotten in a combustion furnace, the carbide glowed brightly, as if burning, and a nearly white powder was obtained. The combustion was imperfect, however, unless the tube was very hot and the ignition prolonged. This refers not merely to the gra-



phitic carbon mixed with the carbide but to the carbide itself. In several experiments the substance withdrawn from the tube, after heating some hours in oxygen, decomposed violently in water. It may be added, as was to be expected, that carbon dioxide had no appreciable action upon the carbide.

*Action of Hydrochloric Acid.*—Hydrochloric acid had no action upon this substance in the cold. When passed over the heated substance it caused it to swell up and assume a dirty gray appearance. A small amount of a liquid, apparently water, collected in the cooler portions of the tube and parts of the carbide fused down in glassy globules and masses. These were soluble in water and were easily shown to be calcium chloride. White fumes were evolved some of which settled as a white solid upon the sides of the tube.

*Action of Chlorine and Bromine.*—When chlorine was passed over fresh carbide in the cold no action was observed. If even a moderate heat was applied, however, the lumps of carbide glowed very brightly, swelled, and fused together. A slight yellowish white sublimate was found in the tube. The fused mass was calcium carbide.

Bromine mixed with air was then passed over the fresh carbide. In the cold no action was observed. On heating, the carbide became red and the smaller pieces glowed. The lumps fused together and bubbles were observed on the surface as if some gas was escaping from the mass. Some condensed matter was found afterwards in the tube, and, on cooling, a peculiar odor was noticed different from that of bromine. The fused mass dissolved readily in water and gave the tests for calcium bromide. Of course in this and the previous experiment the black specks of graphitic carbon were found unchanged. It was easy to distinguish them from the carbide. A few pieces of the carbide were dropped into strong, freshly prepared, chlorine water. There was a very violent disengagement of gas but it was not ignited as reported by Moissan. The gas was inflammable and burnt very much like acetylene. The odor was, however, peculiar. The same experiment was tried several times with a concentrated solution of bromine in water. The action again was very violent but there was no spontaneous ignition of the gas.

Little difference could be detected between this and the action of the chlorine water.

*Action of Acids.*—A piece of the carbide was placed in concentrated pure sulphuric acid. A few small bubbles came off but the action seemed slight. On heating, the action was greatly increased and continued after the removal of the flame. A gas was given off which burned with a luminous flame.

A mixture of sulphuric acid and potassium bichromate acted most violently upon the carbide. There seemed to be a very vigorous oxidation, and several attempts at igniting the gas given off resulted in failure. There could have been very little, if any, acetylene present in it.

Strong nitric acid attacked the carbide with the formation of brown-red fumes. The gas evolved could be ignited and burned with a smoky flame.

Glacial acetic acid decomposed the carbide slowly in the cold.

It may be added that no change was observed on adding a piece of the carbide to some boiling sulphur. On allowing the mass to cool the carbide was regained in its original condition.

*Action of Alkalies.*—A few grams of sodium hydroxide were melted in a nickel dish and a piece of the carbide was added. There was violent action, a gas being given off which burned with a luminous flame and which was taken to be acetylene.

A small amount of sodium dioxide was also melted in a nickel dish. When the carbide was added to this it was rapidly attacked, the action being about the same as in the experiment just mentioned. An inflammable gas was evolved.

In conclusion, we would give due credit to Mr. W. R. Kenan, who carefully verified some of the experiments here recorded.

UNIVERSITY OF NORTH CAROLINA,  
February, 1893.

### NOTE ON THE DETERMINATION OF ZINC.

BY P. W. SHIMER, EASTON, PA.

Received January 24, 1895.

THE manganese in many zinc ores is a disturbing element in the accurate determination of metallic zinc. As is well known the usual separation of zinc from manganese is made by precipitating the zinc as sulphide in a solution which is strongly

acidified with acetic acid. When the manganese is high this precipitate should be dissolved and reprecipitated to purify the zinc sulphide from a little manganese sulphide thrown down with it. To avoid this troublesome reprecipitation I have lately used the following method which does away with the disturbing influence of manganese, and gives results agreeing closely with those obtained by the usual methods.

About eight-tenths gram of the zinc ore is dissolved as usual in hydrochloric acid. In case, as often occurs, there is any insoluble manganese or zinc spinel in the residue, it is necessary to make a fusion. Evaporate the hydrochloric solution to dryness and redissolve and filter if it is desired to determine the silica. In case silica is not to be determined it need not be filtered off. Redissolve in nitric acid (1.20) and evaporate to moist dryness. Add 100 cc. strong nitric acid and precipitate the manganese as dioxide by means of potassium chlorate, as in Ford's method for manganese in iron and steel. Filter through purified asbestos by means of the filter-pump and wash, first with strong nitric acid, then with cold water. Dissolve the manganese precipitate in standardized ferrous sulphate solution and titrate the excess of ferrous sulphate with standardized permanganate solution as in Williams' method for manganese in iron and steel. In this way the manganese is promptly separated, and if desired, determined.

The filtrate from manganese is transferred to a beaker and evaporated to dryness. A little hydrochloric acid is added and again evaporated to moist dryness. On this solution the usual double basic acetate precipitation is made. The united filtrates are evaporated to a bulk of about 300 cc., heated to boiling, removed from the flame, and a rapid current of hydrogen sulphide passed through for one-half hour. The zinc sulphide is filtered off and dissolved in hydrochloric acid and the zinc precipitated, preferably as zinc ammonium phosphate. The precipitate is separated from the paper and weighed as zinc pyrophosphate. The ignition should be done cautiously at a low red heat to avoid fusion of the pyrophosphate and a probable cracking of the crucible at the moment of solidification. In case lime is to be determined in the filtrate from the zinc sulphide, it is

necessary to dissolve and reprecipitate the calcium oxalate, for the first precipitate is sure to contain alkaline chlorides in very appreciable amount. The basic acetate precipitate cannot be used for the determination of alumina, since the manganese precipitate carries down a little iron with it, but apparently no determinable amount of zinc.

### ON THE DETERMINATION OF CANE-SUGAR IN THE PRESENCE OF COMMERCIAL GLUCOSE.<sup>1</sup>

BY H. A. WEBER AND WILLIAM MCPHERSON.

IN the analysis of a great many of the saccharine products found in the markets at the present time, the chemist is confronted with the problem of determining sucrose in the presence of commercial glucose. The official methods for such determinations, either by the use of Fehling's solution alone or supplemented by the polariscope, necessitate, as is well known, the inversion of the sucrose by the action of acids. The accuracy of these methods requires, as one condition, that the acid used in inversion exert no action upon any substance present, other than sucrose, that would in any way affect the reading of the polariscope or would change the power to reduce Fehling's solution. Since commercial glucose, however, contains a greater or less amount of dextrin, and since this undergoes hydrolysis when acted upon by acids, being changed thereby into dextrose, the question arose as to whether such a change might take place during the process of inversion of any sucrose present and thus vitiate the results. The specific rotatory power of dextrin being nearly four times as great as that of dextrose, it is evident that a very slight action would introduce serious errors.

The method of procedure was, first, to determine to what extent dextrin is present in commercial glucose; second, to ascertain whether any change is produced by heating with acids as in the common process of inversion, and finally to discover some method of eliminating this error, if present.

<sup>1</sup> This paper and the one following were sent to Dr. H. W. Wiley to be read before the Association of Official Agricultural Chemists and then transmitted to the editor of this JOURNAL for publication. In consequence of a misunderstanding they were printed instead, in the Proceedings of the Eleventh Annual Convention of the above association. At the request of the authors, and with the consent of the Committee on Papers and Publications, they are now reprinted in full.—Ed.

An examination of the literature accessible upon the subject of the composition of American glucose failed to give any information in regard to the amount of dextrin present.

The report on glucose, Washington, 1884, gives the analysis of some glucoses, but as suggested by Stone and Dickson,<sup>1</sup> improvement or variation in the manufacture since that time would probably cause a change in the chemical composition.

In order to obtain the desired information a number of samples were analyzed. Seven of the samples were kindly sent us by the American Sugar Refining Company, of Chicago, and represent the various grades placed on the market by them. Since this company controls the glucose manufacture in the United States, it is fair to presume that these samples represent, more or less fairly, an average glucose in the market. Two other samples were purchased in Columbus, but analysis showed a composition similar to those sent from Chicago, and inquiry revealed the fact that they had been purchased from the above-mentioned company.

#### METHOD OF ANALYSIS.

A number of different methods have been proposed for the estimation of the constituents of glucose, all more or less objectionable. The shorter ones are only fairly approximate, making no attempt to estimate the amount of the so-called inert or unfermentable carbohydrates (gallisin). The longer methods are probably more exact, but, since the unfermentable carbohydrates are but imperfectly known, it follows that any attempt at finding the exact composition cannot be highly satisfactory.

The following method<sup>2</sup> was selected as giving approximately the relative amounts of dextrose, maltose, and dextrin present.

Twenty-five grams of the glucose were dissolved in water, and the solution made up to 250 cc. With this solution the following determinations were made:

1. *Specific gravity*.—This was determined by weighing with the pyknometer. The Westphal balance was first used, but the results were not so satisfactory as those obtained by direct weighing.

2. *Specific rotatory power*.—This was deduced from the direct

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, No. 6.

<sup>2</sup> See article Sugar, Thorpe's Dictionary of Applied Chemistry.

reading in a 200 mm. tube. The instrument used was the ordinary Schmidt and Haensch polariscope. Its accuracy was tested by a standard plate, kindly loaned by Dr. Wiley.

3. *Cupric reducing power*.—A gravimetric determination was made by adding ten cc. of the solution properly diluted to forty cc. of Fehling's solution previously heated in boiling water until it attained a like temperature and then heating for twelve minutes in water at 100°. The cuprous oxide was filtered through asbestos, well washed, and changed into the cupric form by igniting for fifteen minutes. The weight of the oxide multiplied by 0.4535 gives the amount of reducing sugar present. Experiment showed that good results could be obtained by exercising due care and adhering rigidly to the conditions.

4. *Ash*.—Fifty cc. of the solution were treated with sulphuric acid in a platinum dish until all the carbonaceous matter was burned away, the residue weighed, and the percentage of ash calculated.

The total organic solid matters per 100 cc. were determined by subtracting from the specific gravity of the solution (water = 1,000) the correction due to the ash, and dividing the difference between the result and 1,000 by 3.86. This is based on the assumption that ten grams of carbohydrates dissolved in 100 cc. of water give a solution of sp. gr. 1,038.6 (water = 1,000), also that one gram of ash per 100 cc. gives a specific gravity of 1,008. Now, if in a solution containing ten grams to 100 cc.,

S = total carbohydrates,

(A)d = specific rotatory power for ray D,

K = cupric reducing power in terms of dextrose,

then

$$\text{Maltose (M)} = \left( \frac{(A)d + 1.42K - 195}{27.2} \right) S$$

$$\text{Dextrose (D)} = \frac{SK}{100} - 0.61 M.$$

$$\text{Dextrin} = S - (M + D).$$

It is evident that this method will give only approximate results, since it supposes that the only organic bodies present are maltose, dextrose, and dextrin. However, the results undoubtedly give a fair insight into the amounts of these present.

TABLE NO. I.—GLUCOSES ANALYZED.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Specific gravity.....	1030.60	1031.05	1031.40	1031.18	1033.16
Total solids, grams .....	7.8890	8.01	8.08	8.03	8.56
Specific rotatory power .....	133.33	132.90	120.60	135.40	132.10
Ash, per cent.....	0.18	0.19	0.24	0.21	0.17
Cupric reducing power, per ct.	56.56	57.00	60.60	54.90	56.70
Maltose, per cent .....	54.08	55.44	34.63	54.20	55.40
Dextrose, per cent.....	11.64	11.81	21.24	11.03	14.71
Dextrin, per cent.....	13.18	12.80	24.98	15.09	15.44
	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Specific gravity.....	1033.90	1031.17	1031.48	1033.50	.....
Total solids, grams .....	8.74	8.00	8.11	8.60	.....
Specific rotatory power .....	127.80	149.30	130.31	134.91	40.20
Ash, per cent.....	0.22	0.37	0.29	0.37	.....
Cupric reducing power, per ct.	55.90	43.60	50.65	48.75	.....
Maltose, per cent .....	39.12	47.67	22.30	28.92	.....
Dextrose, per cent .....	25.08	5.81	27.48	24.31	.....
Dextrin, per cent .....	23.18	26.52	31.33	32.81	.....

It is of interest to compare these results with the following, the first three of which are taken from the report on glucose above mentioned. The fourth is the analysis published recently of a product manufactured in England.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.	No. 4. Per cent.
Maltose .....	19.3	7.6	....	36.10
Dextrose ....	36.5	36.5	39.0	18.75
Dextrin .....	29.8	40.9	41.4	25.41

The most noticeable feature of the above analyses is the high per cent. of maltose present and the comparatively low per cent. of dextrose. With a single exception the maltose present exceeds the dextrose, reaching a maximum difference in number 7, which contains 47.67 per cent. maltose and only 5.81 per cent. of dextrose. This particular sample was labeled "Brewers' Extract," the name suggesting a high per cent. of maltose, a characteristic property of the glucoses obtained from Chicago with a malt-like odor noticeable when dissolved in a slight amount of hot water. It will be noticed that the English sample contains almost twice as much maltose as dextrose.

The solid glucose or grape-sugar was not analyzed completely, since the specific rotatory power was so low as to exclude any possibility of the presence of dextrin.

It is of interest to compare the properties of the above glucoses with those examined by Stone and Dickson.<sup>1</sup> The determinations made by them were, in the main, different from those made by us, overlapping, however, in the determination of the specific rotatory power and ash. A marked difference exists in these. The average specific rotatory power of those examined by Stone and Dickson is given as 91.37, while those examined by us showed a variation from 120.6 to 149.3, calculated for ray D. It is possible that the former calculations may have been made for some other ray, and the apparent difference thus diminished. The percentage of ash in the samples examined by us was noticeably smaller, being about one-fourth as great.

The glucoses were next subjected to the same treatment as would be necessary to invert sucrose, if present, *viz.*, heating with acids. It is evident that in order to guard against any hydrolysis of the dextrin or to diminish it, if unavoidable, the temperature to which the acid solution is raised as well as the time during which this temperature is maintained should be no greater than necessary to insure complete inversion of the sucrose. Various methods of inversion have been proposed and various ones are in use by chemists at the present time. The official methods of the agricultural chemists for the years 1890 and 1891 require that the solution to be inverted, mixed with the proper amount of acid, be heated for ten minutes at 68°. This was changed in the report for 1892 and continued in the report for 1893, to heating gradually, reaching 68° at the expiration of ten minutes. This is also the method given by Allen,<sup>2</sup> as well as the one recommended by the "Association des Chimistes."<sup>3</sup>

Three different methods were tried: 1. The above-mentioned or official method; 2. The method recommended by the Association of Official Agricultural Chemists for the years 1890 and 1891, *viz.*, heating at 68° for ten minutes; 3. The German method, which amounts to heating at 67° to 70° for fifteen minutes.

Approximately 26.048 grams of glucose were dissolved in 200 cc. of water. Fifty cc. of this solution mixed with five cc. fuming

<sup>1</sup>J. Anal. Appl. Chem., 7, No. 6.

<sup>2</sup>Allen's Commercial Organic Analysis.

<sup>3</sup>Jour. des Fabr. de Sucre, 32, 1891, No. 35.



hydrochloric acid were heated according to the above-mentioned methods.

TABLE NO. II.—READINGS OF AN APPROXIMATELY FIFTY PER CENT. SOLUTION OF THE VARIOUS GLUCOSEs, BEFORE AND AFTER HEATING WITH ACIDS. TEMPERATURE, 20° C.

[Divisions on cane-sugar scale.]

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Direct reading										
200 mm. tube	85.70	85.50	80.10	86.55	85.30	84.40	90.40	84.90	86.15	42.00
Reading after inversion by first method	85.20	84.85	79.58	86.00	84.90	83.90	89.85	84.20	85.55	42.05
Difference .....	0.50	0.65	0.52	0.55	0.40	0.50	0.55	0.70	0.60	....
Reading after inversion by second method	84.25	83.90	78.75	85.15	84.00	82.90	88.95	83.00	84.45	....
Difference .....	1.45	1.60	1.35	1.40	1.30	1.50	1.45	1.90	1.70	....
Reading after inversion by third method	83.75	83.20	78.10	84.60	83.50	82.15	88.35	82.25	83.75	....
Difference .....	1.95	2.30	2.00	1.95	1.80	2.25	2.05	2.65	2.40	....
Reading after boiling one hour with acetic acid (com.)	85.30	84.90	79.75	86.15	84.85	84.05	89.90	84.30	85.65	....
Difference .....	0.40	0.60	0.35	0.40	0.45	0.35	0.50	0.60	0.50	....

The flasks were carefully calibrated and the duplicates agreed within the error of reading. The results are given in the above table. The solutions were of such a strength that the amount used was the same as would be used in the analysis of a substance containing approximately fifty per cent. glucose.

It will be noticed that in every case, with the exception of No. 10, which contains no dextrin, the reading is sensibly diminished, introducing thereby an error in the estimation of sucrose in the presence of commercial glucose, varying from one-tenth to over two per cent., according to the amounts of the two present and the method of inversion used. While this may not be large enough to cause one to draw unjust conclusions from the analysis of commercial saccharin products, it is nevertheless desirable to eliminate it if possible, or at least to reduce it to a minimum.

Experiments were made to find out the effects of other acids in the hope of finding one that would bring about the inversion without affecting the reading of the glucose. The result showed, however, that even an acid which would not bring about complete inversion would sensibly diminish the reading of the glucose. Thus acetic acid will cause a diminution of reading almost as large as that caused by hydrochloric acid, although it does not *seem* to cause complete inversion. In no case was a smaller error introduced than by the first method above used.

Since the error could not be eliminated by inversion with acids<sup>1</sup> an attempt was made to allow a correction for it. It is evident from the above results that the error is not a widely diverging one, if the samples can be regarded as average ones, and it could be largely diminished by allowing for the mean deviation.

It was necessary, however, before attempting this to find out what the effect would be when the amount of glucose present was varied. Solutions were made containing, approximately, 100, 50, 25, 10, and 5 per cent. of glucose, respectively, and subjected to the action of acids as before. The average results expressed as divisions on cane-sugar scale, were as follows :

	100 per cent.	50 per cent.	25 per cent.	10 per cent.	5 per cent.
Before.....	170.7	85.00	42.35	16.8	8.6
After.....	169.4	84.45	42.15	16.78	8.65
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1.3	0.55	0.2	0.02	....

The results with the various glucoses are sufficiently uniform to warrant one to introduce corrections which, while not eliminating the error, would reduce it to a minimum.

This correction may be easily calculated as follows :

It can readily be seen that the reading due to glucose present may be approximately determined by subtracting from the direct reading three-fourths of the difference between (or sum of) the direct and invert readings (supposing that the temperature be about 20°).

<sup>1</sup> This error would be eliminated by the inversion brought about by O'Sullivan and Thompson's invertase process (*Journal of the Chemical Society of London*, 59, 46). The method is not used to any extent, however, because of the time required as well as the increased labor of analysis.

Let  $R$  equal the reading due to glucose, then the following formula deduced from a graphic representation of the above results will be found to give the correction ( $x$ ) :

$$x = \frac{R-15}{130}$$

This correction must, of course, be subtracted from the numerator ( $a \pm b$ ) in Clerget's formulas. In order to test the accuracy of the above correction a number of mixtures of cane-sugar and glucose were analyzed. Good results were obtained in every instance. The following expressed as divisions on cane-sugar scale, will serve as examples :

Glucose. Per cent.	Sucrose. Per cent.	Direct reading.	Invert reading.	Approximate glu- cose read- ing.	Correc- tion.	Per cent. of sucrose found	
						Without correction.	With correc- tion.
80	20	154.2	126.30	133	0.90	20.82	20.18
50	50	138.4	70.75	87	0.55	50.48	50.11
30	70	120.3	26.23	50	0.27	70.20	70.00
10	90	109.0	11.80	19	0.03	90.15	90.13

The results in Table No. 11 show the necessity of chemists using the same method of inversion. Even in the estimation of pure sucrose it has been shown by a number of chemists that the reading varies slightly according to the method used. In the presence of commercial glucose, however, the variation becomes much greater. When the inversion is accomplished by heating at  $68^{\circ}$  for ten minutes, the difference in reading due to the hydrolysis of the dextrin averages almost three times as great as when the first method is used, while the German method increases this to almost four times. It is barely possible that some of the widely varying results published by the reporter on sugar, in the report of the Association of Official Agricultural Chemists, may owe a part of their discrepancies to these facts.

#### CONCLUSIONS.

Some of the conclusions reached may be summarized as follows :

(1) An error is introduced in the estimation of sucrose in the presence of commercial glucose, due to a slight hydrolysis of the dextrin present during the process of inversion of the sucrose by acids.

(2) This hydrolysis, and consequently the error, is reduced to a minimum when the inversion of the sucrose present is effected by heating for ten minutes, the temperature being gradually raised so as to reach  $68^{\circ}$  at the expiration of this time.

(3) The results with the different glucoses are sufficiently uniform to warrant the introduction of a correction for the mean error.

(4) In order that the results may be comparable, chemists ought to strictly adhere to one method of inversion.

OHIO STATE UNIVERSITY,  
COLUMBUS, OHIO.

### ON THE ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.

BY H. A. WEBER AND WILLIAM MCPHERSON.

WHILE carrying out some experiments with glucose several facts were noted in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger,<sup>1</sup> Jungfleisch and Grimbert,<sup>2</sup> and Ost.<sup>3</sup> Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert<sup>4</sup> claim that acetic acid completely inverts sucrose at  $100^{\circ}$ , and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very percepti-

<sup>1</sup> Boh. Zeit. Zucker, Ind., 1891, 187. Bull. Assoc. Chim., 1892, 559.

<sup>2</sup> Compt. rend., 107, 390, and 108, 144.

<sup>3</sup> Ber. d. chem. Ges., 24, 1636.

<sup>4</sup> Compt. rend., 107, 390.

bly, its specific rotatory power. Exceptions to this view are taken by Maumené,<sup>1</sup> who calls attention to the fact that the invert sugar prepared from sucrose by action of acids is not composed of equal parts of levulose and dextrose. Ost<sup>2</sup> not only denies that acetic acid will produce complete inversion, but also claims that it acts perceptibly upon invert sugar. Ross<sup>3</sup> states, as the result of a number of experiments, that it was found impossible to secure complete inversion even when ten per cent. glacial acid was used and the flask kept immersed in boiling water for forty-five minutes.

Those who claim that acetic acid does not effect complete inversion base their belief upon the fact that invert sugar, prepared by the action of hydrochloric acid upon sucrose, gives a higher reading than the corresponding solution obtained by the action of acetic acid. It was thought that perhaps acetic acid might form some compound with the constituents of the invert sugar, which might affect the reading of the polariscope. Proceeding upon this assumption, attempts were made to decompose such a compound. In the course of these experiments, which were conducted at great length, certain facts were noted which have been systematized in the following:

As stated above, Jungfleisch and Grimbert in particular, have called attention to the fact that the specific rotatory power of invert sugar, prepared by the action of hydrochloric acid on sucrose, is higher than that of the artificially made invert sugar. If, however, as Maumené claims, the invert sugar so prepared is not composed of equal parts of dextrose and levulose, then it is possible that the different readings are due to the peculiar compounds formed. In fact, one would not expect the readings to be identical under such assumptions.

Accordingly, experiments were undertaken to find out, if possible, whether the hydrochloric acid used in inversion affected in any way by its presence the reading of the invert sugar so prepared. Attempts were made in two different directions.

1. Five hundred cc. of a normal solution of sucrose (polariz-

<sup>1</sup> *Journal des Fabricants de Sucre*. Abstract from March 27, 1889.

<sup>2</sup> *Ber. d. chem. Ges.*, 24, 1636.

<sup>3</sup> Report of the Association of Official Agricultural Chemists, Bul. 35, Div. of Chem., Dept. Agr., p. 146.

ing at 99.8) was subjected to inversion in 100 cc. flasks by adding one-tenth the volume of concentrated hydrochloric acid (sp. gr. 1.19) and heating for ten minutes, regulating the heat so that the temperature, 68°, was reached at the end of that time. These solutions were all poured into a large flask and thoroughly mixed, so as to obtain a perfectly uniform solution. Exactly fifty-five cc. of this solution were transferred to a 100-110 cc. flask, the flask filled to the mark with water, the solution thoroughly mixed and polarized. The experiment was repeated with the addition of five cc. of the same acid used in the inversion, previous to filling to the mark with water; again repeated with the addition of ten cc., fifteen cc., and twenty cc., respectively. Since the same solutions, same flasks, and polarizing tubes were used, and the temperature of the solutions did not differ more than 0.5°, corrections being introduced for this variation the chances of error in manipulation were very slight. The following readings, expressed in divisions of cane-sugar scale, were obtained for the various solutions (temperature = 20°):

Invert sugar (containing five cc. of acid).....	— 33.00
Invert sugar + five cc. additional acid .....	— 33.90
Invert sugar + ten cc. additional acid.....	— 34.65
Invert sugar + fifteen cc. additional acid.....	— 35.60
Invert sugar + twenty cc. additional acid .....	— 36.40

The reading is seen to increase with the addition of the acid, thus agreeing with the conclusion of Gubbe.<sup>1</sup> Moreover, the deviations caused by the addition of the different amounts of acid are fairly constant, varying from 0.75 to 0.95, or an average of 0.85. It was hoped that sufficiently uniform results could be obtained to allow the graphic representation, so that an estimate could be made on the effect of the original five cc. of acid added to bring about inversion. Since, however, the addition of a second, third, fourth, and fifth five cc. of acid each increases the reading of the invert sugar approximately 0.85, then we may conclude, with some probability, that the original five cc. of acid which effected the inversion would increase the reading by that amount.

2. Attempts were also made to solve the problem by neutral-

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 2207.

izing the acid present in the invert solution by the action of sodium carbonate.

Bornträger<sup>1</sup> has called attention to the fact that the rotatory power of the neutralized solution is higher than that of the corresponding acid solutions. By the addition of sodium carbonate, however, not only is the acid neutralized, but a corresponding amount of sodium chloride is thereby added. Readings were taken first to find out the effect of the addition of the sodium chloride. Then, by comparing this with the variation caused by neutralization with sodium carbonate, the effect of the acid could be deduced.

Five hundred cc. of inverted sugar solution were prepared as described above. It was found that three and three-tenths grams of pure dry sodium carbonate were necessary to neutralize the acid (five cc.) present in fifty-five cc. of this solution. The experiments were conducted as in the above. Fifty-five cc. of the solution were transferred to a (100-110) flask, neutralized with sodium carbonate, the flask filled to the mark, the solution mixed thoroughly and polarized. The duplicates agreed within the limit of error in reading. The average readings on cane-sugar scale were as follows (temperature = 20°):

	Triplicates.		
	1.	2.	3.
Original solution.....	-33.1	-33.0	-33.20
Original solution + 3.3 grams sodium carbonate (neutral).....	-33.7	-33.7	-33.85
Original solution + 6.6 grams sodium carbonate .....	-36.2	-36.0	-36.30

The last reading was taken in order to compare the effects of the addition of sodium carbonate before and after neutralization. It is thus seen that, while the reading of the normal solution is increased 0.6° by the addition of the necessary amount of carbonate to neutralize the acid, the subsequent addition of a like amount increases the reading 2.5°. Before ascribing this difference in reading to the effect of the acid, it is necessary to find whether or not the sodium chloride, formed by the addition of the sodium carbonate to hydrochloric acid, affected the reading.

Experiments were conducted with the same solution used

<sup>1</sup> *Boh. Zeit. Zucker. Ind.*, 1891, 187.

above. Fifty-five cubic centimeters of the solution were introduced into the 100-110 cc. flask, and the amount of sodium chloride corresponding to three and three-tenths grams of sodium carbonate, or 3.65, added, the flask filled and the solution polarized as before. The average readings on cane-sugar scale, agreeing within  $0.1^\circ$ , are :

Original solution.....	-33.1	-33.15
Original solution + 3.65 grams sodium chloride..	-35.1	-35.10

Since, then, the effect of the sodium chloride was to increase the reading  $2^\circ$ , the acid remaining unneutralized, while the reading was only increased  $0.6^\circ$  by the addition of the same amount of sodium chloride, the acid being neutralized at the same time, the difference  $1.4^\circ$  may presumably be attributed to the action of the acid present.

This result is higher than the one deduced from the direct addition of acid given above, but it is undoubtedly the more correct of the two. It would thus seem that the acid undoubtedly increases the rotatory power, the probable increase of reading being about  $1.4^\circ$  on the direct scale for the normal solution.

Similar experiments were next conducted in order to find out the effect of acetic acid. The strength of the acid used may be inferred from the fact that five cc. of it required for neutralization 3.05 grams of dry sodium carbonate. The normal solution of sucrose was heated at  $100^\circ$  with one-tenth volume of this acid for about one hour, experiments showing that continued heating had but little effect upon the reading. By this treatment a reading for the normal solution was obtained on an average of  $2^\circ$  lower than when hydrochloric acid was used as the agent of inversion. The same solution which gave a reading of  $-33.1^\circ$  when hydrochloric acid was used gave a reading of  $-31.1$  when treated with acetic acid under the above conditions.

Experiments performed to discover whether the subsequent addition of acetic acid would affect the reading, gave the following results, on cane-sugar scale :

Original invert solution (temperature $20$ ).....	-31.10	-31.0
Original invert solution + ten cc. additional acetic acid...	-30.85	-30.8

The second reading is the reading obtained from a solution exactly the same as the first ten cc. of acetic acid being introduced.



It thus appears that while hydrochloric acid increases the reading by its presence, acetic acid decreases it by a small but perceptible amount. This result agrees with Ost, who criticises the statement of Jungfleisch and Grimbert that acetic acid has no effect upon invert sugar. In order to test this further, the acid was neutralized by sodium carbonate and the difference of reading noted. This result, united with the effect due to the introduction of the sodium acetate formed, gave the means of finding the effect of the acid.

The experiments were conducted as in the above, using same solution, same flasks, and same polarizing tubes. The following are the results obtained, on cane-sugar on scale :

Original solution (temperature 20°).....	-31.20	-31.1
Original solution + 3.05 grams sodium carbonate (neutral) ..	-32.65	-32.6
Original solution + (3.05 X 2) grams sodium carbonate..	-34.80	-34.8

A marked difference is noted here as compared with similar experiments with hydrochloric acid. The neutralization of the hydrochloric acid increased the reading only 0.6°, while the neutralization of the acetic acid increased the reading over twice the amount, or 1.5°. The subsequent effects of the sodium carbonate upon the two solutions agree very well, being an increase of 2.5° in the case of hydrochloric acid against an increase of 2.2° in the case of acetic acid. This difference of 0.3° in the reading is accounted for by the fact that 3.3 grams of sodium carbonate were added in the hydrochloric acid solution, while only 3.05 grams were added in the acetic acid solution. If correction be made for this difference, the increase in readings differ only by 0.1°.

It was necessary also to find out the effect of the sodium acetate formed by the neutralization of the acetic acid by sodium carbonate. The readings on the cane-sugar scale were as follows :

Original solution (temperature 20°).....	-31.1	-31.1
Original solution + 4.72 grams sodium acetate....	-32.4	-32.4

The sodium acetate used was the pure anhydrous salt.

It is thus seen that while the sodium carbonate increased the reading 1.5°, the introduction into the original solution of the same amount of sodium acetate as was formed increased the

reading but  $1.3^{\circ}$ . The difference of  $0.2^{\circ}$  must be due to the presence of the acid.

The conclusion that the acetic acid by its presence lowers slightly the reading is confirmed by the fact that by the use of a weaker acid a maximum reading of  $-31.3^{\circ}$  was obtained.

As might be expected the introduction of hydrochloric acid into a solution inverted by acetic acid increases the reading in a corresponding degree.

It is thus shown that the effect of hydrochloric acid upon a solution of invert sugar is to increase the reading, while acetic acid has an opposite effect. Moreover, the experiments show that the probable increase in reading due to hydrochloric acid under the conditions mentioned is  $1.4^{\circ}$ , while the probable decrease in reading due to acetic acid is  $0.2^{\circ}$ . In other words, if these two acids produced the same effects upon being heated with sucrose, there would still be a difference of reading of  $1.6^{\circ}$  due to the presence of the acid. This agrees fairly well with the actual difference observed.

In the light of these experiments it may be of interest to notice the question so often discussed, "Does acetic acid effect complete inversion?" If we suppose that no acid effects complete inversion unless it gives a reading such as that obtained by using hydrochloric acid, then most certainly acetic acid does not invert completely. If, on the other hand, we adopt as the reading of the invert solution the reading of the acid solution, corrected for the effect produced by the presence of the acid, then acetic acid gives more nearly the correct invert reading, and it is correct to affirm that acetic acid does invert sucrose completely.

Finally, the above results indicated that when Fehling's solution is used in the place of the polariscope, it would be a matter of indifference whether acetic or hydrochloric acid was used to effect the inversion of the sucrose. Experiments showed this to be true. Two solutions containing the same amount of sucrose were inverted with hydrochloric and acetic acids respectively. After inversion exactly 11.7 cc. of each solution were required to reduce ten cc. of Fehling's solution. Moreover, when Fehling's solution is used for the determination of sucrose in presence of dextrin or commercial glucose, acetic acid is preferable to hydro-

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chloric acid as the agent of inversion, since the process requires no attention, and the error introduced by the hydrolysis of dextrin is less even when the most favorable method of inversion is used; *viz.*, heating for ten minutes, regulating the temperature so as to reach 68° at the expiration of that time.

OHIO STATE UNIVERSITY,  
COLUMBUS, OHIO.

## METHOD OF DETERMINING CHROMIUM IN CHROME ORE.

BY EDMUND CLARK.

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PROF. STORER and others have suggested the use of nitric acid and potassium chlorate as agents for the oxidation of chromic compounds to chromic acid. Using this suggestion as a basis for the determination of chromium in chrome iron ore, I have experimented with a method which has proved both practicable and accurate.

For complete analysis a half gram sample of the finely ground ore is weighed into a platinum crucible with a capacity of not less than fifty cc. The ore is covered with twenty-five grams of potassium bisulphate and fusion is commenced over a Bunsen burner with very low flame which is protected from air currents by a sheet iron chimney.

To insure complete fusion, and to guard against any loss, the operator must manipulate carefully and watch the operation from beginning to end. At first, the flame should be so low as to fuse the bisulphate very slowly.

After the mass is in a liquid condition, and there is no longer any danger of loss from spattering, the crucible is grasped with a pair of crucible tongs and the contents are run up around the sides, in order to seize hold of any particles of ore which may have become stranded there.

At this stage of the process, the flame may be increased a little so as to cause a tolerable redness of the bottom of the crucible.

At intervals of ten minutes the crucible must be manipulated by the operator as before described. Forty minutes will suffice for complete decomposition of the ore. Pour the contents into a perfectly clean and dry, four to five-inch platinum evaporating

dish, making as thin a layer of the mass as possible. Place the crucible and cover in a twelve-ounce beaker and reserve for the solution.

Cool the contents of the dish quickly by means of a shallow vessel of cold water, which should be immediately at hand. Cover the dish with a suitable watch-glass to prevent loss of particles by the sudden contraction of the cooling mass. When cool, rinse off the watch-glass and add thirty-five cc. of hydrochloric acid (1.20 sp. gr.) and twenty-five cc. of water.

Boil quietly over the flame, keeping the watch-glass on, until the solution is complete, usually requiring about fifteen minutes. Transfer the solution, with care, to the beaker containing the crucible and warm on the steam-bath until the crucible and cover can be washed free from the bisulphate fusion. The solution now occupies about 100 cc.

Let contents practically settle, then decant the clear supernatant fluid into another twelve-ounce beaker and add fifteen cc. more of hydrochloric acid to the residue. Heat on the steam-bath until nothing but silica remains undissolved. Unite solutions and filter, reserving the filtrate and igniting the filter. Weigh as silica.

The filtrate, which should be easily contained in a twelve-ounce beaker, is now rendered slightly alkaline with ammonia.

The dirty, reddish green precipitate consists of the hydroxides of chromium, aluminum, and iron. These are warmed on the steam-bath until the smell of ammonia is faintly perceptible. Filter on a fifteen cm. filter without washing and dissolve the collected hydroxides into the original beaker, with dilute hydrochloric acid. Reprecipitate with ammonia and collect on the same filter as before, washing carefully three times with hot water, combine the two filtrates, and in the united solution determine lime and magnesia by any good method.

Transfer the filter containing the precipitated hydroxides to a four and one-half inch porcelain evaporating dish and cover with a five-inch watch-glass. Add fifty cc. of nitric acid (1.42 sp. gr.) and heat gently over a Bunsen flame. From time to time carefully add potassium chlorate with a small glass or porcelain spatula. The addition of this reagent is attended with small

explosions, which should be reduced in violence, as much as possible, by adding small quantities and not too frequently. Great care should be taken here to avoid loss from spattering.

The gradual oxidation may be noticed by the changing of the dirty green color of the emulsion to a clear orange-red solution. The organic matter of the filter-paper has been completely oxidized along with the chromic hydroxide. The complete oxidation is easily detected, but a small excess of potassium chlorate is added to insure it. The chromium now exists as chromic acid.

Transfer the solution to a twelve-ounce beaker, making up to about 150 cc. with water, and precipitate the iron and alumina with ammonia. Filter into a sixteen-ounce beaker without washing. Dissolve the precipitate on the filter with warm, dilute nitric acid and wash thoroughly, allowing the solution to run into the beaker in which the precipitation was made. Reprecipitate with ammonia and throw the precipitate on the same filter, allowing the filtrate to be caught in the same beaker as was the first filtrate. Separate, and determine, the iron and alumina by any good method.

The ammoniacal filtrate contains the chromium as ammonium chromate. Acidify with hydrochloric acid and add a sufficient quantity of strong sulphurous acid water to completely reduce the chromium. The clear, bright green color imparted to the solution is an indication of the complete reduction.

The excess of sulphurous acid must be driven off. This may be done by boiling, but it may be accomplished in a highly satisfactory manner by leaving the open beaker remain on a steam-bath over night.

Upon the complete removal of the sulphurous acid, the solution is rendered just alkaline with ammonia, with a final addition of three or four drops in excess. Stir well with a glass rod and heat over a lamp until the smell of ammonia is only faintly perceptible. We have, now, a precipitate of chromium hydroxide ready for filtration. Filter on a 12.5 cm., filter and allow it to drain without washing out the beaker or washing the precipitate. After the precipitate has drained, wash it carefully back into the beaker by inverting the funnel and using warm water. Add more warm water and stir to insure complete solution of all alkaline salts.

Throw the precipitate back upon the same filter and wash three times with hot water. Drain, dry, and ignite in a platinum crucible and weigh as chromium sesquioxide.

Another method of determining the chromium in the yellow solution of ammonium chromate, and one which many chemists may consider the more expedient, is as follows :

Moderately acidify the ammonium chromate solution with acetic acid and warm. Add an excess of a clear solution of plumbic acetate and allow the precipitate of plumbic chromate to settle in a warm place for several hours ; then collect on a weighed filter (previously dried at  $100^{\circ}$  C.) and wash with cold water.

Dry at a temperature of  $100^{\circ}$  to  $110^{\circ}$  C. and weigh. The increase of weight is the weight of the plumbic chromate, from which the percentage of chromic oxide may be calculated.

The choice given to either of these methods for the final precipitation of chromium is purely arbitrary.

In a future article the method employed in the estimation of chromium in chrome steel and ferro chrome will be dealt with.

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### NEW BOOKS.

PROCEEDINGS OF THE ELEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, BULLETIN No. 43, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY, EDITED BY DR. H. W. WILEY. pp. 403. Washington : Government Printing Office. 1894.

This bulletin issued annually through the courtesy of the U. S. Department of Agriculture, contains, as usual, the results obtained by the various reporters appointed by the Association, a general discussion of their reports, and a complete summary of the methods of agricultural chemical analysis which are now almost universally used in this country and which have official recognition.

Some sixty chemists participated in the meeting, and the very full discussions denote a lively interest in the work. For the first time a committee was appointed to consider the changes of method recommended by the various reporters and to approve the same before submitting them for action. Most of the changes recommended were approved by the committee. It is, however, gratifying to note that these changes were, as a rule, unimpor-

tant. The analyses made for nitrogen by the official methods agree closely and the only change made was in the wording of the Gunning method modified to include nitrates. The Tiemann-Schulze method for nitrates alone, was adopted as a provisional method until a better could be found although the reporter was instructed to continue his efforts in this direction. The use of two and five-tenths per cent. acid and alkali was dropped from the method of crude fiber determination leaving the one and one-fourth per cent. solution alone official. The dilute ammonia for washing magnesium pyrophosphate was made more definite in strength by prescribing a two and five-tenths solution, and Pemberton's volumetric method for estimating phosphoric acid appears quite promising and bids fair, after further study, to become official. No co-operative work was done on dairy products either from satisfaction with our present methods or from lack of interest. One or two changes in the methods for potash were made for the sake of uniformity. The report on soil and ash analysis was quite full and an unusually large number of chemists took part in the investigation. This is the more surprising as the analyses are very tedious and a large outlay of time was necessary. The results too are unsatisfactory both on ash and on the soil solutions, in view of which the question may well be raised as to how our general methods of mineral analysis would compare in the hands of different analysts. The changes of method adopted for soil analysis have already been printed in this JOURNAL, 16, 792. One noteworthy point brought out by the reporter as a result of his work and that of other chemists is that the best glass is fully as good as the best porcelain for the solution of silicates and that no appreciable error will be introduced by its use. A reporter on tannin was appointed for next year and provisional methods adopted. The reporter on fermented liquors was also instructed to include the analysis of distilled liquors in his next year's investigations. Nearly 150 pages of the bulletin are covered with abstracts of agricultural chemical articles and represent the year's work of the abstract committee.

There seems to be a growing conservative feeling among the members in regard to alterations of method as a result of some

past mistakes. This is to be commended but should not be carried so far as to become prohibitive. The best results will be reached when good judgment and conservatism go hand in hand. Many will doubt the wisdom of the change made in the constitution itself, prohibiting any change, except by unanimous consent, in the methods of fertilizer analysis until an opportunity shall have been given all official chemists to try the same. This gives to any one member a power to delay action which many will think should be held by the majority alone. The appointment of reporters for two years, and associates who shall fit themselves to become reporters on the special lines of work, should meet the approval of all chemists and may be far-reaching in its results. The Secretary of the Association has not felt himself impowered to make any alterations whatever in the wording of the methods; and it is pleasing to learn that a special committee has been appointed to rewrite the methods and put them in creditable English.

There is a growing feeling in the Association that it is reaching the point where it can well enlarge its scope. In the past it has confined itself strictly to analytical processes, but the desire seems to be increasing for investigations along the line of availability in fertilizer and food material and to make more of a study of proximate constituents. General dissatisfaction is expressed with the present "citrate-soluble phosphoric acid," "crude fiber," "nitrogen-free extract," etc., and it is to be hoped that dissatisfaction will lead to renewed investigations. The Association has an additional and unlimited field of usefulness for itself along this line.

C. L. PARSONS.

BIBLIOGRAPHY OF ACETO-ACETIC ESTER AND ITS DERIVATIVES. BY PAUL H. SEYMOUR, M.S., INSTRUCTOR IN CHEMISTRY, LAKE FOREST UNIV. Smithsonian Miscellaneous Collections, No. 910. pp. 147. Washington: Smithsonian Institution. 1894. Price 75 cents.

The rapidly increasing literature of aceto-acetic ester makes this volume of great value. The author has given brief abstracts of the articles that have appeared upon the subject of the bibliography from 1840-1891, "omitting what had no relation to aceto-acetic ester." The abstracts are clear, and full enough to



accomplish their time-saving purpose. Misprints are infrequent. On page 107, however, we find "uvitic acid" and "carbuvitic acid" instead of uvic acid and carbuvic acid. Excellent author and subject-indexes accompany the abstracts.

L. B. H.

REPORT ON THE EXTENT AND CHARACTER OF FOOD AND DRUG ADULTERATION, BULLETIN NO. 41, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 64. Washington: Government Printing Office. 1894.

EIGHTH ANNUAL REPORT OF THE DAIRY AND FOOD COMMISSIONER OF OHIO. BY F. B. MCNEAL, COLUMBUS, OHIO.

FIRST ANNUAL REPORT OF THE COMMISSIONER OF AGRICULTURE OF NEW YORK. BY F. C. SCHRAUB, ALBANY, N. Y.

A COMPILATION OF THE PHARMACY AND DRUG LAWS OF THE SEVERAL STATES AND TERRITORIES, BULLETIN NO. 42, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 152. Published by order of Congress. 1894.

There seems to be a growing interest among our legislators and among the general public in reference to pure foods and drugs. Many of the states and, in fact, a majority have laws making druggists responsible for the drugs they sell, requiring that only pure dairy products shall be sold, and placing a standard on commercial vinegar, but in most instances the laws have simply served to adorn the statute books. Much work has been done to arouse the public, and in view of the strict control exercised on adulteration in most other advanced countries, it is surprising that it has not met with more immediate success. The cause has undoubtedly been injured by grossly exaggerated articles claiming general impurity of all our food products, but enough adulteration, proved by actual analysis by competent chemists, is now coming to light to demand immediate enlargement and enforcement of our laws.

The chief records of recent opinions and analyses will be found in the above reports. Among the replies received by the special agent of the Department of Agriculture and recorded in Bulletin No. 41, will be found many statements by some of our best chemists. These are, in general, noteworthy for their conservative tone but, as a rule, each has had some form of adulteration come under his personal notice, and those whose duties have caused them to investigate the matter, give many examples of foods,

drugs, and dairy products, which they have found badly falsified.

It seems to have been left, however, for the Food and Dairy Commissioner of Ohio to make the first really important move in this matter, and the results tabulated in his Eighth Annual Report make extremely interesting data for chemists at large. It is true that in Massachusetts, New York, Wisconsin, and a few other states, a good many cases have been prosecuted for violation of the laws, but the examination of food products have been made mainly to prevent the watering and skimming of milk and the substitution of oleomargarine for butter. In Ohio, however, there is a much broader clause in the law, to the effect that "any article made of or sold under the name of another article, or falsely branded, or upon which art has been used to conceal inferiority, or in which there is fraud or deceit," shall be deemed illegal. Upon this basis the efficient Commissioner, Mr. F. B. McNeal, appears to have attempted, without fear or favor, to purify the food stuffs of all kinds sold within his jurisdiction. His work has been eminently successful, the results are widely quoted, and several states are apparently about to appoint Commissioners to follow his example. Among the substances found adulterated, baking-powder, buckwheat flour, butter, cider, coffee, chocolate, condensed milk, fruit-butter, honey, jelly, oleomargarine, olive-oil, preserves, quinin pills, vinegar, and wine, were impure in at least half of the samples analyzed, and in some cases there was not a particle of the substance itself present. Other noteworthy examples of impurity were in pepper, milk, mustard, cream of tartar, etc., and it will be specially interesting to note that butter added to oleomargarine is considered also in the light of an adulteration. The analyses are printed in more or less detail and will be useful to any chemist for reference. All, however, will deplore the fact that no methods, or references to methods used, are given, and also that the word "about" is not more frequently printed to modify the results. The statement of exact percentages of butter-fat in oleomargarine, of the various impurities in coffee, of foreign fats in butter, of the water added to milk, etc., are impossible, and when so directly made are misleading to the general public and cause much trouble for conservative chemists when they are quoted against them in the

courts. With this exception there is little to criticise in the report, and it is certainly to be hoped that many others showing equal results will follow.

The First Annual Report of the Commissioner of Agriculture of New York is practically a continuation of the reports of the previous dairy commissioner. The report contains many analyses, but they are confined almost wholly to dairy products, oleomargarine, and vinegar. In the sub-report of the cheese instructor, will be found a full and detailed account of the investigations on cheese planned by Mr. Van Slyke, the chemical features of which have already been published by him in this JOURNAL, 15, 605, 635, 645, and 16, 712, and the Bulletins of the New York Experiment Station. One important feature of the report is the summary of the laws of all the states on foods and dairy products. From this summary it appears that the requisite standard for milk varies between twelve per cent. and thirteen per cent. solids, eighty-eight per cent. and eighty-seven per cent. water, and three per cent. to three and one-half per cent. fat, and condensed milk must be made by the evaporation of standard milk without addition of other matter. The standard for vinegar varies between a minimum of four per cent. to four and one-half per cent. acetic acid and cider vinegar must have at least two per cent. cider vinegar solids. Vinegar cannot contain any sulphuric acid, lead, copper, or other deleterious substance. In regard to oleomargarine, Massachusetts and Ohio forbid its sale if colored in imitation of yellow butter. In New Hampshire, Vermont, West Virginia, and Minnesota, it must be colored a bright pink. Pennsylvania, Virginia, Missouri, and Delaware, prohibit its sale altogether. There seems to be no detailed laws in regard to other food products.

The bulletin of the Department of Agriculture on Pharmacy and Drug Laws will serve mainly as a place of reference for legal information. Most of the states now require all persons compounding or dispensing drugs to pass rigid examinations and receive certificates of registration. Poisons are restricted in sale and must generally be labeled in red letters, and sales entered in a special poison registry book. Many of the states make the druggist responsible for the purity of the drugs he sells, while

others make him responsible only when he is aware of their character.

Altogether the four reports show a growing interest in the subject of adulteration and an increasing tendency to legislate on the subject. It would appear, however, that no general results will be obtained until there is some national law which will regulate the trade between states in adulterated goods. When such a law is passed we may soon expect an efficient control and a consequent greater field for chemical usefulness and employment.

C. L. PARSONS.

**KRÄFTE DER CHEMISCHEN DYNAMIK.** VON DR. LUDWIG STETTENHEIMER. pp. 88. 8 vo. Frankfurt am Main: H. Bechhold. 1895. Price, 6 m.

These three lectures appear to have been held before a mixed audience, containing probably more mathematicians or physicists than chemists. They are of a polemical nature, against the molecular hypothesis, but they confine themselves to general problems and do not touch at all upon the purely chemical relations, such as those of isomerism, polymerism, and organic reactions. As far as can be extracted from a somewhat involved line of argument every substance whether a mixture, compound, or simple substance is to be regarded as a homogeneous individual as long as chemical reaction does not take place. There is no separation into molecules, but every atom reacts upon every other atom in a purely mechanical way, as do the celestial bodies; atoms near one another simply influencing each other to a larger degree than those further apart. The introduction of any new atoms, whether of the same or of another sort, disturbs the equilibrium which can be restored either by an equal distribution of the new atoms throughout the mass without disturbing the relative positions of the old atoms, or by a total rearrangement of the positions.

In the discussion of the solid state, views similar to those of the late T. Sterry Hunt are developed, but they are extended over the liquid and gaseous condition as well.

All disturbances of the relative positions of the atoms are considered chemical reactions, whether these be performed by simply separating them mechanically, as in pouring half of a liquid into another vessel, or by what are ordinarily known as chemical changes or, by electrolysis, change of aggregation, etc. The

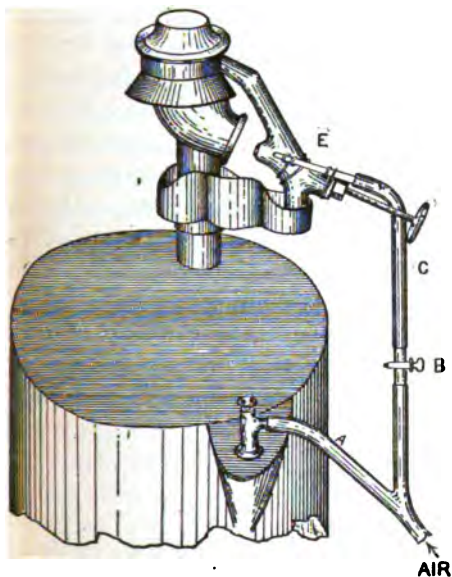
various modes of energy are all considered to depend exclusively upon relative changes of position between the atoms. Such views as those of Williamson's hypothesis are discarded because atoms are not even momentarily associated into real molecules.

It is difficult to criticise the reasoning, inasmuch as it is based upon the most general forms of phenomena and deals with these in the largest possible fashion, dealing with infinitesimal disturbances in very large masses. Until the subject is applied to purely chemical reactions in greater detail no gain can be perceived in these new assumptions. The grounds upon which the molecule, as a physical identity, is abandoned, appear to be somewhat trivial.

M. L.

### NOTES.

*An Improvement on the "Dangler's Laboratory Lamp."*—The enclosed sketch illustrates an improvement on the "Dangler's Laboratory Lamp."



B. Glass stop-cock.

C. Rubber tubing.

E. Glass tip kept in place by a copper wire.

After using this lamp for about two years it began to burn with a smoky flame. I then introduced a small jet of air into the flame as shown. By the help of the glass stop-cock the air is regulated, while a steady pressure is exerted on the gas-line through the side tube A. In this way the lamp will burn all day with a uniform and most perfect flame, strong or weak, as desired; no gas-burner can possibly give better satisfaction.

The air-blast is obtained from a Bunsen filter-pump, which is supplied with water from an artesian well.

ANDREW LUNDTEIGEN.

*Spurting in Cupellation.*—Dr. H. G. Torrey, of the N. Y. Assay Office, writes to the *Engineering and Mining Journal*, under date of February 26, that a comparative test of old and new cupels has been made with reference to their liability to spurt and thereby cause loss in the muffle. The test was made on 1,000 each of cupels less than one week old and about one year old. "In each case the number of cupels that spurted was the same, being only about one per cent. \* \* \* The result of all the different experiments [which we have made] is that the spurting is due not to moisture, but to the escape of gas arising from the decomposition of impurities remaining in the cupel, and that this gas not only takes time but a high heat to expel."

*A Substitute for Hydrogen Sulphide* is found by Schiff and Tarugi in thioacetic acid made by acting on glacial acetic acid with phosphorus pentasulphide. The solution, for students' use, is made by dissolving the acid in a slight excess of dilute ammonia, and is given out in bottles having a pipette holding about two cc. thrust through the cork. About one-half to one gram of substance, dissolved in hydrochloric acid, is treated, while hot, with one and one-half to two cc. of a thirty per cent. solution of the above ammonium thioacetate. The sulphides are completely separated; even arsenates are completely decomposed. *Ber. d. chem. Ges.*, 27, 3437.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### HENRY BRADFORD NASON.

Henry Bradford Nason, Professor of Chemistry and Natural Science at the Rensselaer Polytechnic Institute, Troy, N. Y., died of apoplexy, at his home, on January 17, 1895.

Professor Nason was a former president of the American Chemical Society, and for very many years an active, interested, and energetic member.

During the early days of the Society, long before it had acquired its present established footing, he stood as one of its staunch supporters, and never despaired of its eventual and permanent success; a faith which to-day has become reality.

Those who were so fortunate as to know Professor Nason personally, will remember with pleasure that scientific attainments were associated in him with a cheerful and kindly nature, eminently qualified to win many and lasting friends.

He was the son of Elias and Susanna (Keith) Nason, and was born at Foxborough, Norfolk County, Mass., June 22, 1831. In November, 1841, he moved to North Bridgewater, Mass., the native place of his mother, who died the year previous. In 1843 he attended a school for boys kept by Mr. Savory at Newburyport, Mass. From 1844 to 1847 he attended the Adelphian Academy at North Bridgewater, now Brockton, Mass. In December, 1847, he entered Williston Seminary, Easthampton, Mass., graduating in 1851. He entered Amherst College and graduated in 1855. September 1, 1855, he sailed from New York to London on the ship Amazon, having a passage of thirty-five days. He travelled through Holland, Belgium, up the Rhine to Frankfort

and then to Göttingen, where he was matriculated as a student of philosophy October 24, 1855. While connected with the university he devoted his time to chemistry, mineralogy, and geology, and attended lectures on physics and botany, graduating in the Summer of 1857. He spent a short time at Heidelberg and Freiburg and then visited Berlin, Paris, and London. He spent the Winter of 1857-58 in teaching at the Raymond Collegiate Institute, Carmel, Putnam County, N. Y. In April, 1858, he was appointed professor of natural history in the Rensselaer Polytechnic Institute. In the Summer he declined an appointment as professor of chemistry and natural science in Oahu College, Hawaiian Islands. He accepted an appointment to the same chair in Beloit College, Wisconsin, in September, 1858, and spent a part of each year there, the remainder of the time at Troy, until 1866, when he resigned the position at Beloit to accept the professorship of chemistry and natural science at the institute, which position he held until his death.

From 1855 to 1857, while connected with the university at Göttingen, during vacations he made the tour of Europe. In the Spring of 1860 he travelled through the southern portion of the United States. He sailed for Europe in July, 1861, and travelled through Great Britain, and afterward went to Italy, Sicily, and southern France, spending considerable time in the study of volcanic phenomena. He spent the Summer of 1872 in California, Nevada, and Idaho. In the Autumn he made a second visit to California, visiting the mining regions of Colorado and Utah. In 1875 he made a third trip to California, visiting the Yosemite, northern California and Nevada. He spent the Summer of 1877 in visiting northern Europe, Finland, and Russia.

In 1877 Professor Nason was appointed by President Hayes juror for the United States Government at the Paris Exposition and was assigned the department of mineralogy and metallurgy.

In 1884 he visited northern Europe and the fiords and glaciers of Norway, extending his travels to the North Cape.

Professor Nason published "Inaugural Dissertation on the Formation of Ether," 1857; "Table of Reactions for Qualitative Analysis," 1865; translated and revised "Wohler's Handbook



of Mineral Analysis," 1868; "Table for Qualitative Analysis in Colors," 1870; edited Elderhorst's "Manual of Blowpipe Analysis," 1873; fourth and fifth editions of the same, 1875-76; edited "Manual of Blowpipe Analysis and Determinative Mineralogy," 1880; compiled "Semi-Centennial Catalogue of the Rensselaer Polytechnic Institute," 1874, and edited "Proceedings of the Semi-Annual Celebration" of the same institution, 1874; edited "Biographical Record of the Officers and Graduates of the Rensselaer Polytechnic Institute," 1886.

In 1857 he received the degree of A.M. and Ph.D. from the Georgia Augusta University, Göttingen; in 1864 the honorary degree of A.M. from Amherst College; in 1880 the honorary degree of M.D. from the Union University of New York, and the same year the honorary degree of LL.D. from Beloit College, Wisconsin. He has been elected fellow of the American Association for the Advancement of Science, fellow of the London Chemical Society, fellow of the Society of Chemical Industry, England, member of the American Chemical Society, corresponding member of the New York Academy of Science, member of the American Institute of Mining Engineers, member of the Troy Scientific Association, honorary member of the Albany Institute, member of the Norske Turistforenings, Christiana, Norway; elected member of the University Club, 1883, and of the Union League Club, New York City, 1886.

W. P. MASON.

## METHODS FOR THE DETERMINATION OF MANGANESE.<sup>1</sup>

By W. S. THOMAS.

Received February 11, 1895.

FOR some time no satisfactory method for the rapid determination of manganese has been in use in this laboratory; all proposed schemes have been, from time to time, successively tried and none have withstood the tests under all conditions.

With the great demand now made for chemical analyses by which metallurgical and manufacturing processes are controlled, it has been no small part of the chemist's work to devise rapid methods for making these determinations, so necessary for the information of the metallurgist and manufacturer.

<sup>1</sup>This and the paper following it are reprinted from the Bulletin of the Missouri Mining Club, published at the Missouri School of Mines, Rolla, Mo.

In order to supply this need, every rapid method now in use and generally known or published, has been introduced into the course of instruction known as Technical Analysis in this laboratory.

During the past two years the determination of manganese has been attempted by using a method published in the *Journal of Analytical and Applied Chemistry* by A. H. Low, but so far as the method has been applied in this laboratory it has proven of no value, owing to the low results obtained.

For the purpose of arriving at a satisfactory conclusion in regard to the Low method, a series of experiments were begun, using manganese carbonate, and manganese sulphate, from which most of the water of crystallization was driven off and the sample kept in a corked tube. In order to check the volumetric work the metallic content of both salts was carefully determined by gravimetric analyses, in which the manganese was precipitated as manganese ammonium phosphate, ignited, and weighed as pyrophosphate.

This method gave very closely agreeing results by duplicate analyses of the respective salts, the filtrate in each case being tested for manganese by means of ammonium sulphide and only mere traces of manganese found.

A standard solution of potassium permanganate was made in which 6.312 grams of potassium permanganate were dissolved in two liters of distilled water, and a solution of 11.46 grams of  $C_2H_2O_4 + 2H_2O$ , (oxalic acid), in one liter of distilled water, kept well corked and away from the light.

In obtaining an experimental standard, ten cc. of the oxalic acid solution were taken and five cc. of sulphuric acid added, and the whole titrated with standard potassium permanganate, one cc. = 0.0056 gram of iron, the strength of the oxalic acid being calculated from the data obtained.

It was found that ten cc. of oxalic acid reduced 20.1 cc. of the standard potassium permanganate, one cc. of which equals 0.0011 gram manganese, based on the equation  $10FeSO_4 = K_2Mn_2O_8$ . Therefore one cc. oxalic acid equals 0.002211 gram manganese.

By calculation based upon the equation (Low's)



126 parts of oxalic acid equal fifty-five parts of manganese. Knowing the weight of oxalic acid in one cc. of solution and introducing this into the proportion, one cc. of oxalic acid solution was found to be equivalent to 0.005 gram manganese.

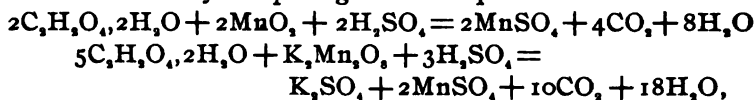
From these two methods we obtain two entirely different strengths, neither of which give satisfactory results, as will be seen by calculations based upon titrations, made according to Low's instructions.

A half gram of manganese sulphate, which gave 34.64 per cent. manganese by gravimetric analysis, was taken and made up to 500 cc.; fifty cc. were taken for each titration, zinc oxide was added in the usual way, and bromine water to precipitate the manganese as manganese dioxide, the excess of bromine boiled off, solution filtered, the precipitate well washed with hot water, and the filter with its contents replaced in the flask where the precipitation was made; fifty cc. of dilute sulphuric acid added and a measured volume of oxalic acid run in from a burette; the excess of oxalic acid determined by treating with the standard potassium permanganate. Nine titrations by Low's method gave the following results:

No.	$C_2H_2O_4 \cdot 2H_2O$ added.	Excess of $K_2Mn_2O_8$ .
1	10 cc.	13.6 cc.
2	10 "	13.6 "
3	10 "	13.4 "
4	10 "	13.6 "
5	10 "	13.8 "
6	10 "	13.5 "
7	10 "	13.8 "
8	10 "	13.8 "
9	10 "	14.0 "

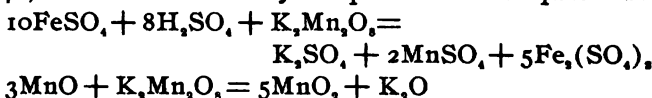
Taking a mean of the excess as 13.6 cc. of potassium permanganate, and multiplying by 0.0011 (one factor of the strength of the permanganate) and dividing by 0.002219 the strength of one cc. of oxalic acid in terms of potassium permanganate, we obtain the amount of oxalic acid oxidized by the 13.6 cc. of potassium permanganate, which, subtracted from ten cc. gives the number of cubic centimeters of oxalic acid oxidized by the manganese dioxide derived from the sample. Multiplying this by 0.0055+ and correcting for one gram, we obtain 35.64, which is

one per cent. above the gravimetric result as the per cent. of manganese in the sample. The factor  $2\frac{1}{2}$  used in this calculation is obtained by comparing the two equations:



from which is readily seen, that the strength of one cc. of oxalic acid in terms of potassium permanganate is  $2\frac{1}{2}$  of its strength in terms of manganese dioxide, from which we can derive a strength for oxalic acid based on experiment and not on calculation, as set forth in another place.

Titrating the same sample of manganese sulphate by Volhard's method, in which the strength of the potassium permanganate in terms of iron equal to 0.0056 gram, is multiplied by the factor 0.2946, which is obtained by comparison of the equations:



(in which  $\text{K}_2\text{Mn}_2\text{O}_8 = 10\text{FeO}$  and  $3\text{MnO}$  respectively) the following results were obtained: One-half gram of substance taken and made up to 500 cc. and fifty cc. taken for each titration.

No. of titration.		Cubic centimeters of $\text{K}_2\text{Mn}_2\text{O}_8$ used.
1	50 cc. solution.	10.3
2	50 cc. solution.	10.3
3	50 cc. solution.	10.3

Multiplying this result by 0.2946 and correcting for one gram we get thirty-four per cent. manganese or 0.64 per cent. less than by the gravimetric analyses.

The methods were both tried upon a sample of manganese carbonate, which gave, by means of manganese pyrophosphate, forty-five per cent. of manganese. Several samples of one-half gram were taken and a few titrations made from each with the following results. Six titrations by Low's method gave

No.	$\text{C}_2\text{H}_2\text{O}_4, 2\text{H}_2\text{O}$ added.	Excess of $\text{K}_2\text{Mn}_2\text{O}_8$ .
1	10 cc.	12.9 cc.
2	10 "	12.6 "
3	10 "	13.0 "
4	10 "	12.3 "
5	10 "	12.3 "
6	10 "	12.9 "

Throwing out No. 3, the average volume of potassium permanganate reduced by the excess of oxalic acid equals 12.6 cc. and applying the same calculations as before, we obtain 41.03 per cent., or four per cent. less than by gravimetric analyses.

Eight titrations by Volhard's method gave the following results:

No.	Solution.	K <sub>2</sub> Mn <sub>2</sub> O <sub>8</sub> added.
1	50 cc.	13.5 cc.
2	50 "	13.5 "
3	50 "	13.5 "
4	50 "	13.4 "
5	50 "	13.5 "
6	50 "	13.4 "
7	50 "	13.5 "
8	50 "	13.5 "

When corrected for one gram these titrations give 44.54 per cent. manganese, or 0.46 per cent. less than the gravimetric analyses.

The results obtained with Low's method are in one case approximate, but, when the same manipulations are applied to as much as one-half gram of substance, the result is nearly fifty per cent. too low. Theoretically the method is perfect, but I have been unable to obtain the theoretical results in practice, and in so far as this is the important feature, the method has proved worthless in my work.

Volhard's process is very rapid and simple in its application. The manganese should be in the form of a proto salt, which is the form obtained by the procedure in decomposing an ore. Iron is removed by means of zinc emulsion,  $3\text{ZnO} + \text{Fe}_2\text{Cl}_6 = \text{Fe}_2\text{O}_3 + 3\text{ZnCl}_2$ , which converts the iron into insoluble ferric oxide by vigorous shaking.

This having been done, the solution, precipitate and all, is made up to 500 cc.; fifty cc. is taken out by means of a pipette, placed in a twelve-ounce flask, 250 to 300 cc. of hot water added, heated to boiling, standard potassium permanganate run in, and the solution shaken after each addition of potassium permanganate. A bulky brown precipitate of manganese dioxide is formed and the pink color of the solution is destroyed until the manganese is all oxidized to manganese dioxide, when a drop of

the permanganate imparts a pink color to the solution. A few trials will enable the operator to ascertain this point with accuracy and rapidity.

This work was conducted more for the purpose of ascertaining the values of the methods when working with the rapidity which is required in actual practice, than for absolute accuracy, to 0.01 or 0.001 per cent. I have no doubt that Volhard's process can be made to check closer than 0.64 or 0.46 per cent. respectively, of the metallic content of an ore, but in practical metallurgical analyses, it is not always practicable to exercise the necessary precautions. The method is capable of wide application, and where rapidity is essential, is sufficiently accurate in most, if not all cases.

### THE WET ASSAY FOR COPPER.

By R. S. DULIN.

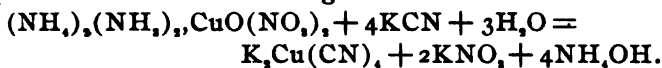
Received February 11, 1895.

IT seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say, that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are :

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper, when the percentages fall below two per cent. I have made no particular study of this method, and as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact, that when a solution of potassium cyanide is run into an ammoniacal solution of copper the blue color is discharged. The reaction is as follows :



This method is fully described in Furman's Manual of Practical Assaying. The following precautions should always be carefully observed. 1. The bulk of the liquid titrated should always be uniform. By inattention to this an error of from two to three per cent. is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about three per cent. is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as five per cent., or even more.

These precautions are general and must always be carefully observed, in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated, upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing, an aliquot part of the solution ; if the solution be not thereby made very dilute, the error is so slight that it may be neglected. If salts of manganese are present, the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from twenty-five to as much as fifty cc., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	11.0 "	0.6 cc.
0.05	0.02	11.7 "	1.3 "
0.05	0.03	12.3 "	1.9 "
0.05	0.04	12.9 "	2.5 "
0.05	0.05	14.0 "	3.6 "
0.05	0.06	16.1 "	5.7 "
0.05	0.07	18.9 "	8.5 "
0.05	0.08	21.6 "	11.2 "
0.05	0.09	24.3 "	13.9 "

These results show that there is a gradual increase of about six-tenths cc. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of twenty per cent., when the increase, though larger, about two and seven-tenths cc., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	10.6 "	0.2 cc.
0.05	0.02	10.8 "	0.4 "
0.05	0.03	11.1 "	0.7 "
0.05	0.04	11.6 "	1.2 "
0.05	0.05	12.0 "	1.6 "
0.05	0.06	12.4 "	2.0 "
0.05	0.07	13.5 "	3.1 "
0.05	0.08	14.5 "	4.1 "



These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent usually found associated with copper, it must be removed, if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

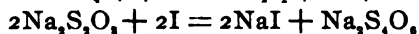
The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's Manual of Assaying. In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present, it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice, by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; three cc. of nitric acid are then added to the flask and boiled to dissolve the copper, the solution is then treated with ammonium hydroxide as in the usual way and titration is made with the usual solution of cyanide.

This method has been very carefully tested and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior district and in foreign countries, where it is regarded with much favor. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt

from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions :



The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's Manual of Assaying, and I only desire to call attention to the necessity for attending to the following precautions :

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of two to three per cent. 2. The solution should be titrated cold. 3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper. 4. The presence of bismuth clouds the end reactions. My experience with the modification of this method, in which the copper is first precipitated with aluminum foil convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages; this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method

The electrolytic method is perhaps the most highly favored in this country. It has the reputation for greatest accuracy. It requires more time than either of the other, but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work after solution is effected, the copper should be precipitated with hydrogen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added twenty cc. of strong nitric to about 150 cc. of solution. This holds up the other metals, but a stronger cur-

rent is required to precipitate all of the copper and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then redissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20.15 per cent. of copper, as determined by a large number of analyses, made by several different assayers, and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be twenty-eight per cent., while the per cent. of copper in the ore was 30.18 per cent.

The results obtained by the cyanide method were respectively 20.15 per cent., 27.95 per cent., and 30.20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20.25, 28.35, and 30.3 per cent. By the electrolytic method, the same substances gave, respectively, 20.045, 28.15, and 30.05 per cent.

These results justify the statement that the iodide method with the aluminum modification gives results usually one-tenth to three-tenths per cent. too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.

## ON THE STANDARDIZATION OF SULPHURIC ACID.

BY F. S. SHIVER.

Received February 16, 1895.

**M.** WEINIG<sup>1</sup> has described a method for the standardization of sulphuric acid by means of weighing the  $(\text{NH}_4)_2\text{SO}_4$  obtained by mixing an accurately measured quantity of the sulphuric acid solution with an excess of ammonia, evaporating, drying, and weighing. His method of procedure is as follows: To an accurately measured quantity of the sulphuric acid solution, ammonia in slight excess is added, the solution evaporated to dryness, dried for half an hour at  $115^\circ$ —

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 204, 205; *J. Chem. Soc.*, 64, 2, 145.

120° C., cooled in a desiccator, and weighed as ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ). Recognizing the tendency of ammonium salts to decompose, especially when in aqueous solution and in the presence of heat, I was rather uncertain whether, by the mode of procedure just described, one would obtain the normal sulphate. Watts says concerning ammonium salts: "Their aqueous solution, when exposed to the air (still more rapidly when evaporated) generally loses ammonia, an acid salt or a normal salt mixed with excess of acid, being formed; hence, in crystallizing an ammonium salt, ammonia must be added occasionally during the evaporation." I therefore decided to make some experiments in this connection since it was of primary importance that the salt weighed should be the normal sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ). Four portions of twenty cc. each of the  $\frac{N}{4}$  sulphuric acid solution were accurately measured out and treated as directed by Weinig.

Results were as follows:

I.	0.3987	gram	sulphur	trioxide	in	twenty	cc.	of	$\frac{N}{4}$	sulphuric	acid.
II.	0.3989	"	"	"	"	"	"	"	"	"	"
III.	0.3990	"	"	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"	"	"
Aver.	0.3990	"	"	"	"	"	"	"	"	"	"

These residues tested with delicate litmus seemed to be feebly acid; to further test this point, four portions of twenty cc. each of this same acid were measured out and treated as follows: The acid solution was made alkaline with ammonia in excess and evaporated down to dryness; the dish was then removed from the bath and its contents thoroughly moistened with strong ammonia water, preferably 0.96 sp. gr.; this will avoid the spattering occasioned by the use of concentrated ammonia water and is just as effective as the latter; the dish was then replaced on the bath and allowed to remain until its contents appeared quite dry, then removed and dried for half an hour at 110°–120° C., cooled in a desiccator, and weighed; the drying repeated for another half hour at the same temperature, cooled, and weighed; no further loss of weight occurred from this second drying in these experiments but I think it safer to weigh the second time, else one is left in doubt as to the thorough desiccation of the ammonium sulphate. The results by this method of treatment are as follows:

I.	0.3996	gram	sulphur	trioxide	in	twenty	cc.	$\frac{N}{4}$	sulphuric	acid.
II.	0.4001	"	"	"	"	"	"	"	"	"
III.	0.3993	"	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"	"
Average	0.3996	"	"	"	"	"	"	"	"	"

These residues tested with delicate litmus were neutral. It will be seen then that the results by the second mode of treatment are slightly higher in nearly all cases than those obtained by the first method described. In further proof of the slight decomposition that takes place when an aqueous solution of ammonium sulphate is evaporated to dryness, I took one of the residues obtained by the second method just described and added about as much water as there was present in the first evaporation; this solution was evaporated to dryness, dried as already described, cooled, and weighed; the weight of ammonium sulphate before adding water and second evaporation was 0.6591 gram, after adding water and second evaporation 0.6581 gram, a loss of 0.0010 gram ammonium sulphate; the amount of sulphur trioxide calculated from this weight of ammonium sulphate, viz., 0.6581 gram, will be seen to agree quite closely with the results secured by the first method described, in which there seems to be some slight decomposition of the ammonium sulphate.

Therefore from these experiments there seems to be some slight decomposition produced when an aqueous solution of ammonium sulphate is evaporated to dryness and in order to be sure to obtain the normal salt, it is necessary, in my experience, to moisten thoroughly with ammonia water the residue as has been described and then to dry and weigh in the manner directed. The decomposition noticed and the error in results occasioned by it is slight, though the results in most cases are lower than those obtained when precaution is taken to prevent this decomposition by moistening with ammonia water as has been described.

The results of this method compared with the precipitation by barium chloride and weighing as barium sulphate are quite close and satisfactory. In one cc. of  $\frac{N}{4}$  sulphuric acid there was found by the barium chloride method 0.02007 gram sulphur trioxide equivalent to 0.00855 gram ammonia. The ammonium sulphate

method, as carried out by myself, gives 0.01998 gram sulphur trioxide equivalent to 0.00851 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.35 cc. of which equals twenty cc. of the  $\frac{N}{4}$  sulphuric acid) is equivalent to 0.003396 gram ammonia by the barium chloride method and by the ammonium sulphate method as carried out by myself 0.003380 gram ammonia.

Another solution of  $\frac{N}{4}$  sulphuric acid was tested by the two methods.

In one cc. of the solution there was found by the barium chloride method 0.01977 gram sulphur trioxide equivalent to 0.008421 gram ammonia.

The ammonium sulphate method, as carried out by myself, gives 0.019895 gram sulphur trioxide equivalent to 0.008474 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.25 cc. of which equals twenty cc. of the  $\frac{N}{4}$  sulphuric acid) is equivalent to 0.003351 gram ammonia by the barium chloride method, and 0.003372 gram ammonia by the ammonium sulphate method, as carried out by myself. I think that as a method of standardization the ammonium sulphate method will be found very simple and accurate and for these reasons should commend itself to those analysts who make use of sulphuric acid as their standard acid.

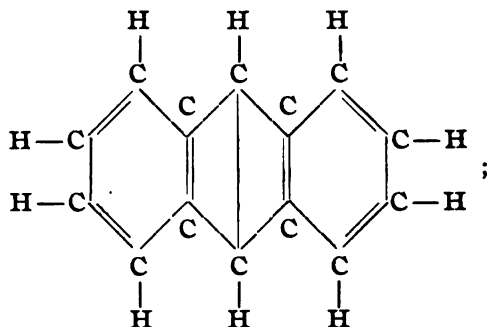
February 11, 1895.

## ON SOME EXPERIMENTS IN THE ANTHRACENE SERIES.

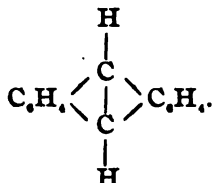
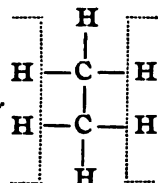
BY C. E. LINEBARGER.

Received March 4, 1895.

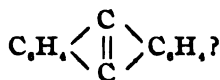
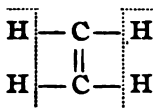
TO anthracene is generally assigned the formula :



it may also be thought of as ethane, in which four of the hydrogen atoms have been replaced by the two bivalent radicals, phenylene:

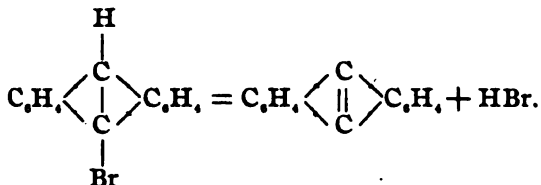


In both the formulas, the two middle atoms of carbon are bound directly together, and the hydrogen atoms in immediate union with them—in the so-called  $\gamma$ -position,—exhibit a characteristic behavior. The question arises, can not the  $\gamma$ -carbon atoms become bound together doubly, so as to form a hydrocarbon, which may be regarded as derived from ethylene,



The question appeared to possess enough importance to merit investigation, and in what follows an account is given of the experiments carried out in seeking an answer to it.

The first attempt to prepare such a compound as the above was made by a study of the action of heat upon mono-brom-anthracene. It seemed likely that through the application of heat hydrobromic acid would be formed by the combination of the hydrogen and bromine in the  $\gamma$ -position, and the bonds of carbon thus set free would unite with each other, as shown in this equation:



Ten grams of pure mono-brom-anthracene were heated in a small round-bottomed flask provided with a delivery-tube. The

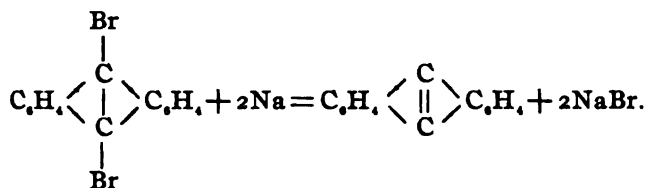
flask was set upon a sand-bath, and its upper part protected from the direct action of the heat by means of a shield of asbestos board. A thermometer was inserted through the cork, reaching almost to the bottom of the flask, so that its bulb was completely immersed in the heated substance. Heat was applied slowly, and it was found that hydrobromic acid gas commenced to pass off at  $250^{\circ}\text{C}.$ , and the evolution became quite brisk at  $280^{\circ}$  to  $300^{\circ}$ . The temperature was not, however, allowed to rise higher than  $300^{\circ}$ , and when the evolution of gas had nearly ceased, the heating was discontinued. The neck of the flask was full of yellowish crystals, while in its bottom there remained a black resinous mass from which no crystalline substance could be obtained. The crystals were dissolved in hot benzene, and the solution, on cooling, became filled with tablets resembling those of anthracene. These, by a second crystallization from a mixture of alcohol and benzene, were obtained in a state of purity. Their melting-point was found to be  $210^{\circ}$  to  $212^{\circ}$ , which is that of anthracene; they were also, like anthracene, soluble with dark green color in concentrated sulphuric acid; there is no doubt, therefore, that the product of the reaction, that is, as far as anything crystallizable is concerned, is anthracene. The hydrogen necessary for its formation must have been taken from the resinous mass.

Experiments were now carried out on the action of alcoholic potash on the brominated compound of anthracene. Three grams of mono-brom-anthracene were heated with twenty grams of alcoholic caustic potash in sealed tubes at temperatures varying from  $100^{\circ}$  to  $250^{\circ}$ . No reaction seemed to occur at temperatures below  $150^{\circ}$ ; the products obtained at higher temperatures were always about the same. When the tubes, which were always filled with crystals, were opened, considerable quantities of inflammable gases escaped; the crystals, when washed free from caustic potash and purified by crystallizations from alcohol, melted at  $207^{\circ}$  to  $211^{\circ}$ . This point of fusion together with the appearance of the crystals—small glistening tablets possessing fluorescence—and the characteristic green coloration with strong sulphuric acid is sufficient evidence that the product is merely anthracene.



The action of solid caustic potash in like circumstances gave also nothing but anthracene.

An investigation was now made of the action of metallic sodium on di-brom-anthracene dissolved in different liquids. It was thought that, perhaps, the sodium would abstract the halogen from the anthracene compound, and that union would then occur between the two  $\gamma$ -carbon atoms, thus:



A molecule of di-brom-anthracene, together with nearly enough benzene to dissolve it, was sealed up in a tube with somewhat more than four molecules of sodium, and heated at  $100^\circ$  for eight hours; no reaction took place. When heated, however, for the same length of time at  $125^\circ$ , the contents of the tube had turned black. The tube was opened, and the dark-colored crystals purified by repeated crystallizations from mixtures of benzene and alcohol. The crystallizable product finally obtained was nothing else than di-brom-anthracene; the reaction which had supervened had evidently not effected the desired synthesis.

The reaction was now tried with xylene as solvent. Ten grams of di-brom-anthracene were dissolved in sixty grams of xylene—which had been distilled over sodium—and an excess of sodium added. The solution was kept vigorously boiling for twenty hours, an inverted condenser being used. The dark colored products of the reaction were filtered off hot, and the crystals, that soon separated out from the filtrate, repeatedly crystallized out of benzene until a pure product was obtained. This showed itself, by its melting-point ( $207^\circ$  to  $210^\circ$ ), fluorescence, and coloration with concentrated sulphuric acid, to be anthracene. The sodium did, indeed, remove the bromine, but so unstable a molecule was formed that a portion of the product was destroyed in order to yield hydrogen for the formation of anthracene.

The above are the simplest and most direct methods for realiz-

ing the proposed synthesis. Whether others will succeed where these have failed is an open question; at any rate the theoretical importance to be attached to the possibility of existence of such

a hydrocarbon as  $C_2H_4 \begin{matrix} C \\ || \\ C \end{matrix} C_2H_4$ , makes it desirable that all the methods be tried.

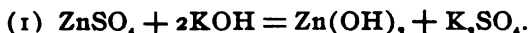
CHICAGO, March 1, 1895.

### ON THE REACTION BETWEEN ZINC SULPHATE AND POTASSIUM HYDROXIDE.<sup>1</sup>

By C. E. LINEBARGER.

Received March 4, 1895.

It is customary in books on analytical chemistry to represent the precipitation of zinc hydroxide from solutions of its sulphate by means of potassium hydroxide, and its redissolution by the action of an excess of the alkali by these two equations:



These equations are, however, far from corresponding to actuality, and it seems really deplorable that chemists in their desire to formulate compounds and balance equations should, by symbolical representations on paper, give the impression of having duly explained such a reaction as the above, which even a superficial examination shows to vary considerably with the temperature, dilution, and relative masses of the components.

The general scheme followed out in this preliminary study of the reaction of the two salts in question consisted in the addition to a constant quantity of zinc sulphate, varying quantities of potassium hydroxide, the total volume and temperature of the

<sup>1</sup> This investigation was begun in 1888 in the chemical laboratory of the Northwestern University at the suggestion and under the guidance of Prof. A. V. E. Young. It had been the intention to study the reaction between zinc sulphate and potassium hydroxide in a manner analogous to that in which Prof. Young had made "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydrate," published in the Proceedings of the American Academy of Sciences and Arts, June 10, 1885. Only certain preliminary experiments, however, had been performed when I left the University, and the research has not received further attention at the hands of Prof. Young or myself. While these preliminary experiments can be said to be but a small part of the work necessary for the elucidation of the problem of the chemical equilibria presented by the system of zinc sulphate, caustic potash, and water, yet they possess a certain interest, especially for analytical chemistry, which may warrant their being made known.

system being kept constant in all experiments, and the immediate analysis of the precipitate. The details were as follows: 36.2 cc. of a solution containing two grams of anhydrous zinc sulphate were brought into a graduated 500 cc. flask, and diluted to about 225 cc. The required quantity of potassium hydroxide solution was also diluted to about the same volume and added to the zinc sulphate. The flask was briskly shaken, the volume of the mixture made up accurately to 500 cc., again well shaken, so as to insure a homogeneous mixture, and the whole thrown upon a large dry filter. Portions of fifty cc. each of the filtrate were taken and analyzed, duplicate determinations being made of zinc and sulphuric acid, and in some cases of potassium. The sulphuric acid was determined volumetrically by precipitation with barium chloride according to Wildenstein's method, the zinc, volumetrically by precipitation with sodium sulphide, lead acetate in alkaline solution being used as indicator, and the potassium, gravimetrically as potassium sulphate. From the analysis of the filtrate, it is easy, since the total amounts of substances present in the system are known, to calculate the composition of the precipitates.

Before the communication of the results of these experiments, it is well to mention a couple of experiments, designed, one to find out the amount of fixed alkali necessary to just precipitate all of the zinc, the other to ascertain how much was required to redissolve the precipitate. In the first experiment, potassium hydroxide was added, from a burette, to a solution of zinc sulphate of known concentration, until the resulting solution was alkaline, care being taken that the same amount of zinc sulphate and about the same amount of water was present as in the precipitation experiments. It was found that one molecule of anhydrous zinc sulphate is precipitated by 1.62 molecules of potassium hydroxide.

In the second experiment, potassium hydroxide was added from a burette to a solution containing one molecule of anhydrous zinc sulphate until the precipitate, at first formed, redissolved, 13.2 molecules of the alkali being required. In this case, however, the dilution was somewhat different from that in the precipitation experiments.

In Table I are given the results of the experiments :

TABLE I.		
I.	II.	III.
No. of Ex.	Mols. KOH to one mol. $\text{ZnSO}_4$ .	Per cent. ZnO in precipitate.
1	0.25	17.11
2	0.50	35.10
3	1.00	68.08
4	1.62	100.00
5	2.00	98.49
6	3.00	96.79
7	5.00	89.76
8	7.00	68.87
9	13.20	0.00

If these data be plotted in a curve, the axis of abscissae being the number of molecules of potassium hydroxide to one molecule of anhydrous zinc sulphate, and the axis of ordinates being the per cent. of zinc oxide in the precipitate, it is seen that the curve at first ascends almost in a straight line to ordinate = 100, and abscissa = 1.62 (the point of complete precipitation), and then falls to ordinate = 0, and abscissa = 13.2 (the point of re-solution) in a perfectly regular manner.

## CHEMICAL BRICK FOR GLOVER TOWERS.

BY IRVING A. BACHMAN.

Received January 15, 1895.

**I**N the last year, Chemical Brick for Glover Towers, from a new locality,<sup>1</sup> have been placed upon the market, which in physical appearance and color are like the famous Blue Welch Brick, and in quality rival them.

Specific gravity, 1.93. Hardness, 7.5.

Color, umber blue. Fracture, blue.

Silica,	$\text{SiO}_2$ .....	72.11 per cent.
Alumina,	$\text{Al}_2\text{O}_3$ .....	20.58 "
Iron oxide,	$\text{Fe}_2\text{O}_3$ .....	5.48 "
Calcium oxide,	$\text{CaO}$ .....	0.92 "
Magnesium oxide,	$\text{MgO}$ ....	0.54 "

A whole brick placed in the bottom of working Glover Tower, acid at 62° B. and 310° F., lost as follows :

<sup>1</sup> Manufactured from the Aiken, S. C., clays.

Weight of brick.....	2934.22	grams.
" " " at expiration of 1 week.....	2933.01	"
" " " " " 2 weeks.....	2931.92	"
" " " " " 3 " .....	2929.41	"
" " " " " 4 " .....	2928.36	"
" " " " " 5 " .....	2927.11	"
" " " " " 6 " .....	2925.26	"
" " " " " 7 " .....	2923.99	"
" " " " " 8 " .....	2922.78	"
" " " " " 9 " .....	2921.53	"
" " " " " 10 " .....	2920.05	"

## Whole brick immersed in boiling

	66° B. sulphuric acid, 5 hours, lost 0.08 per cent.
Same reweighed " 60° B. " " 5 " " 0.07 "	
" " " 50° B. " " 5 " " 0.06 "	
" " " 47° B. " " 10 " " 0.06 "	

## A piece from interior of brick immersed in boiling

	66° B. sulphuric acid, 5 hours, lost 0.15 per cent.
Same reweighed " 50° B. " " 5 " " 0.07 "	
" " " 50° B. " " 5 " " 0.07 "	
" " " 47° B. " " 5 " " 0.04 "	

The edges still remained firm and sharp.

AUGUSTA, GA., January, 1895.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[Continued from page 260.]

At about this period several processes were introduced for the preservation of wood against decay; and claims were made that these were also valuable for rendering wood unflammable.<sup>1</sup> These processes consisted essentially in the introduction into the pores of wood of metallic salts in solution, which combined with the nitrogenous matter present to form insoluble, non-fermentable compounds, and therefore removed sources of decay.

The chief methods employed were kyanizing or impregnation with mercuric chloride; burnettizing or impregnation with zinc chloride, using a three per cent. solution; boucherizing or injection of copper sulphate, using a one per cent. solution; and

<sup>1</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

Beer's process of impregnating with borax. All of these methods give partial protection against combustion. With regard to their availability, expense and the evolution of poisonous vapors, when exposed to heat, militate against the use of corrosive sublimate. Copper sulphate, which can be absorbed to the extent of twenty kgms. per cubic meter of wood, is far inferior to many other salts as a fire protective; it colors the wood blue when exposed to atmospheric conditions, and in common with the mercuric salt, corrodes iron nails and bolts. Zinc chloride is more efficient, although in common with the two preceding salts it affects the tenacity and elasticity of wood. Borax seems to be more free from the objectionable features just enumerated, and more recent experiments have shown that its protective power is far superior to that of the copper or zinc salts, although inferior to that of sodium tungstate and ammoniacal salts.

The operation of impregnation in closed vessels by the use of a vacuum was devised by Samuel Benthams in 1794. It was successfully employed in France by Bréant and Bethel in 1830, and later in England for the purpose of kyanizing and burnettizing, as well as in connection with Payne's process.<sup>1</sup> In boucherizing, the copper sulphate solution is usually forced longitudinally from the butt to the trunk of a tree, just after it is felled, by an ingenious arrangement, involving the use of rubber caps and an elevated tank.<sup>2</sup>

In 1855 Salomon's process<sup>3</sup> of treatment with aluminum sulphate and calcium chloride, already described in connection with textile fabrics (p. 147) was applied to wood with some little success.

During this same year Maughams process<sup>3</sup> of treating wood with a mixture of sodium phosphate and ammonium chloride, and Jackson's process, based on the combined use of zinc and ammonium salts, were both submitted to critical tests by Sir Frederick Abel,<sup>4</sup> who found neither as cheap or as efficient as sodium silicate. Abel reported at length to the English Board of Ordnance on the advantages offered by the use of sodium silicate, which he had recommended at an earlier date for use in the

<sup>1</sup> Frémy, *Dict. de Chimie*, 20.

<sup>2</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

<sup>3</sup> Amer. Arch., loc. cit.

Crimea to render huts fireproof, and which was used in 1856 in camp huts at Aldershot for the Royal Engineers. By applying first a coat of silicate, then a coat of lime, and finally a second coat of silicate, Abel obtained a covering which resisted rain and showed no tendency to crack, shrink, or detach itself from the wood. The cost was one cent for five square feet. Later reports to the board made by Abel in 1870 and 1872 state that the efficiency of this protective was totally unaffected by time. In 1881 he also reports that sodium tungstate, already employed for fabrics, may be successfully used for wood, but that it offers no advantages over the sodium silicate process. It is absorbed by wood at the rate of fifty-six kgms. per cubic meter.

Patera, who studied the subject very extensively, recommended in 1871,<sup>1</sup> the use of magnesium borate for wood, finding it fully equal to sodium tungstate. He urged also very strongly the use of a mixture of one part strong ammonia and two parts gypsum, especially for roofing. Severe tests applied to this protective yielded such satisfactory results that the Austrian Minister of Finance recommended it for all government buildings where woodwork was exposed. Patera also advises the use of a coating of one part of ammonium sulphate, two parts gypsum, and three parts water. Another protective covering recommended by him is obtained by first coating wood twice with a saturated solution of three parts of alum and one part of copperas, and then applying a coat of clay mixed in copperas solution.

The successful use of sodium silicate led to the employment of various siliceous paints. One devised by Vilde and Schambeck<sup>2</sup> seems to have given good results. Its composition is pulverized glass twenty parts, pulverized porcelain twenty parts, pulverized stone twenty parts, quicklime ten parts, waterglass thirty parts. The thick syrup is applied with a brush and hardens quickly.

Ransome's siliceous paint,<sup>3</sup> introduced in 1871, consisted of a mixture of pure quartz and waterglass. After application it was coated with calcium chloride in order to render it perfectly insoluble. It has not been used of late years.

Another process involves the application of three coats of dilute

<sup>1</sup>Loc. cit.

<sup>2</sup>Sc. Amer. Cyclop. of Receipts, p. 217.

<sup>3</sup>Amer. Arch., loc. cit.

waterglass, then of two coats of the same mixed with powdered glass; finally of one of thick waterglass.<sup>1</sup> Other preparations consist simply of more or less dilute waterglass, to which zinc oxide or ferric oxide has been added.<sup>1</sup> A most important modification of the simple silicate is that known as cyanite<sup>1</sup> and prepared by introducing aluminum hydroxide into waterglass, so that it is practically a basic aluminum silicate. It is a perfectly colorless liquid, and is applied with a brush. The cyanite is manufactured in England, and is employed in the English War Department by the Woolwich Arsenal, and by the Department of Railroad Inspection. That the product is variable would be indicated by Helbig's analysis<sup>2</sup> in 1888, when he found nothing present but waterglass.

Among other recent preparations is the ignifuge of Martin<sup>3</sup> of France (1880) used for impregnation, and composed of ammonium chloride fifteen parts, boric acid six parts, borax three parts, water 100 parts.<sup>1</sup> Another French preparation is that of Vendt and Herard,<sup>4</sup> 1885, also for impregnation. It consists of alum twelve parts, borax five parts, sodium thiosulphate three parts, potassium sulphate ten parts, water seventy parts. Somewhat peculiar are the following combinations, also used in France;<sup>5</sup> the first a solution of lead sulphate in neutral tartrates; the second an ammoniacal solution of a mixture of calcium acetate and calcium chloride. Brocher's preparation,<sup>1</sup> manufactured near Dresden, and used to some extent in Germany, is of unknown composition, and involves the use of three different liquids in the course of the application of the several coats. Objection has been made to it for this reason, as well as on account of the tendency of the solutions to solidify before use.

The general recognition of the utility of protective coatings led gradually to the extended use of asbestos. E. G. Erichsen,<sup>6</sup> of Copenhagen, in 1881, devised a new protective which consisted of a soluble silicate, metallic oxides, and lime, with ten to twenty

<sup>1</sup> Boudin et Donny, Rapport.

<sup>2</sup> Archiv. f. Hygien, 1888, III.

<sup>3</sup> Troost, Bull. de la Soc. d'Encouragement, 1880, p. 384.

<sup>4</sup> Génie civ., 6, 227.

<sup>5</sup> Frémy, Dict. de Chimie, 10.

<sup>6</sup> Amer. Arch., loc. cit.



per cent. of asbestos. It was applied with a trowel and formed a sort of fire-proof enamel which could be washed with water. Erichsen's preparation was extensively used in Europe, both on the continent and in England.

A further step forward was made in 1883, by C. J. Mountford,<sup>1</sup> of Birmingham, England, who brought out a preparation which consisted of asbestos ground and reground in water, sodium or potassium aluminate and waterglass. When liable to exposure to atmospheric agencies, it receives, further, a certain amount of oil driers and gummy matters and sometimes zinc oxide or barium sulphate. The United Asbestos Co., of England, has manufactured this product on a large scale for ten years, and it has been extensively employed, especially in England. Among other important edifices treated with it are the Parliament Buildings, the British Museum, South Kensington Museum, the Crystal Palace, various theaters, Royal palaces, etc. The cost of this material is eighteen cents per kilogram, and 100 kgms. suffice to cover, with three coats, a surface of fifty-four square meters, so that the cost per square meter is about thirty-three cents. It is a thick, gray product, easily applied, presents a satisfactory appearance when used alone on wood, and furnishes an excellent basis for the application of other paints.<sup>2</sup>

This represents probably the best type of protective coating, thus far devised. There are also two other English preparations of some repute, the nature of which is apparently analogous to the above; Bell's asbestos paint and Blane's fire-proof and water-proof paint;<sup>3</sup> while, in America, a single firm manufactures an asbestos paint.

Such is the history of the different methods of restricting the combustion of wood which have been presented during this century.

Let us next note the means devised to test comparatively the value of the diverse materials recommended.

#### TESTS FOR FIRE-PROOF PREPARATIONS.

In Versmann and Oppenheim's extended investigation on protectives for textiles,<sup>3</sup> the study was carried on in such a way as

<sup>1</sup>Amer. Arch., loc. cit.

<sup>2</sup>Boudin et Donny, Rapport.

<sup>3</sup>Report to the British Association, 1859.

effectually to eliminate one after another of the salts experimented upon until a small group was left, the efficiency of each member of which, under varying conditions, was satisfactorily demonstrated. The usefulness of impregnation by sodium tungstate is easily illustrated by exposure to a flame of strips of cotton cloth, some of which have been soaked in a tungstate solution, while others are in the ordinary condition. The merits of the different protectives for wood, as each one in turn came before the public, until a recent date were usually tested by application to a small hut or the like, within which an active fire of very combustible material was started. Such was the custom of Sir Frederick Abel<sup>1</sup> in his series of experiments already referred to.

Some thirty years ago Professor Pepper, of London, made comparative tests on four salts, strongly recommended for impregnating wood, and as a result placed them in the following order, the most efficient first:<sup>2</sup>

1. Ammonium phosphate.
2. Sodium tungstate.
3. Borax.
4. Alum.

The most thorough and valuable study in this field was made in 1887 by two Belgian chemists, Professors Boudin and Donny, of the University of Gand (Ghent) at the request of the Belgian Minister of Public Works.<sup>3</sup> They submitted to rigorous comparative tests all of the preparations then in vogue, some nineteen in number, and it is to be regretted that their exhaustive report has not been reproduced *in toto* in our journals.

P. Lochtin,<sup>4</sup> in 1893, introduced a simple and easy, if not perfectly exact method of testing, which he applied to about fifty chemical compounds, and brought out several interesting facts.

We will consider first his more elementary methods, taking up later the more improved ones of Boudin and Donny.

Lochtin used strips of thick filter-paper fifty cm. long and five cm. broad, which are soaked in solutions of the substances submitted to experiment, usually a series for each substance of five-

<sup>1</sup> Amer. Arch., loc. cit.

<sup>2</sup> Sc. Amer. Cyclop. of Receipts, p. 217.

<sup>3</sup> Rapport sur les procédés destinés à assurer l'inflammabilité des bois, Gand, 1887.

<sup>4</sup> Dingley's poly. Jour., 290, 230.

tenths, one, two, three and five-tenths, five, ten, fifteen, and twenty per cent. solutions of the anhydrous compound. After being hung on lines and drying at ordinary temperature, the lower ends, where greater quantities accumulate, are clipped off. When insoluble precipitates are to be obtained in the paper, it is first soaked in a solution of the soluble salt, then dried, then soaked in a solution of the precipitating reagent, dried, washed, soaked for six to twelve hours in water, washed, and finally dried. The strips are then folded lengthwise, and while held horizontally, with the folds beneath, kindled at one end. Observation then shows whether the foreign substance hinders or helps combustion, and what is the minimal relative weight of a salt or the minimal strength of its solution, necessary to render the paper unflammable.<sup>1</sup>

Experiment indicates that different substances, although in solutions of equal strength, are retained unequally by the paper; the amount retained increasing in proportion to the insolubility or ease of crystallization of a compound. Very soluble substances are absorbed in almost equal proportions. It is also worthy of note that apart from compounds which are practically store-houses of oxygen, as the chlorates, there are substances which distinctly favor combustion, the alkaline sulphates for example. As illustrations of Lochtin's method, a strip soaked in a twenty per cent. solution of sodium sulphate is kindled at one end. It is observed that it burns easily and readily to the end, as readily as if no foreign matter were present. Again, four strips of paper soaked in ammonium chloride solutions, *a* in a twenty per cent. solution, *b* in a five per cent. solution, *c* in a two per cent. solution, and *d* in a one per cent. solution, are in turn held in the flame. No propagation of flame is shown by *a*; *b* shows a small flame, which is extinguished quickly on removal from the source of heat; *c* yields a larger flame, which burns for about five cm. after removal; and *d* furnishes a still larger flame, which burns to the end. It is evident that the use of a two per cent. solution affords partial protection, and of a five per cent. solution, full protection against inflammability. I have found in personal experience an advantage in using for elementary tests the thin slips of pine wood about eight cm. long and one cm. wide, easily

<sup>1</sup> *Dingler's Poly. Jour.*, 290, 230.

obtained from any tobacconist. These are preferable to Lochtin's strips, as they can be used for testing protective coverings as well as solutions; and in the case of the latter the distribution of the foreign substance throughout the strip is more uniform. The experiments conducted before you, illustrate the relative resistance imparted by a number of the preparations already enumerated.

A third method of comparative testing was devised by Boudin and Donny.<sup>1</sup> A cylinder of light iron rods forty cm. long and twenty-five cm. in diameter is mounted upon an horizontal axis so that it can be easily kept in rotation. Beneath this cylinder is a series of five Bunsen burners, consuming 1000 liters of gas hourly. The wood used for the experiments is in the form of rectangular sticks thirty-nine cm. long and fifteen mm. square. After treatment by injection or painting, bundles of four sticks of each preparation—the individual sticks kept apart by light wedges—are attached by wire to the rods of the cylinder, parallel to its axis, and at equal distances from each other. A bundle of sticks which have not been treated serves as point of comparison in each charge of the cylinder. The row of lamps is next lighted, and the cylinder turned at the rate of six revolutions per minute, so that all of the bundles are uniformly and evenly exposed to the action of the flame. The time is then noted at which each bundle takes fire, or is seriously affected by the heat; and when the combustion of a bundle becomes sufficiently active to affect its neighbors, it is removed. As an example of the working of this method the following series of tests may be quoted from the Belgian report:

Wood not treated took fire at the end of one and three-fourths minutes.

Wood treated with zinc sulphate or alum, at the end of three and one-half minutes.

Wood treated with ammonium sulphate or copper sulphate at the end of five minutes.

Wood treated with borax, or boric acid, or Martin's ignifuge, or Brocher's preparation, at the end of eight minutes.

<sup>1</sup> Rapport.

Wood treated with sodium tungstate, at the end of ten minutes.

Wood treated with calcium chloride or ammonium chloride, at the end of fifteen minutes.

Wood treated with waterglass alone, or with lime, or with powdered glass and kaolin, or cyanite, or the Bell, Blane, or United Asbestos Co. preparations, or ammonium phosphate, at the end of thirty to forty minutes.

The two latter were charred throughout without the production of flame.

A still more rigorous and decisive test has been devised by Boudin and Donny,<sup>1</sup> one which places the experimenter as nearly as possible in the conditions which ordinarily precede the outburst of a conflagration; *viz.*, the production of a flame of greater or less intensity in immediate contact with inflammable material; such as happens when an oil lamp is overturned, a box of matches is kindled by the gnawing of an inquisitive rat, or the like.

The test is simple in its nature, and depends, as in the preceding method, upon the use of wooden rods subjected to a protective treatment. A convenient size is that of twenty cm. in length and fifteen mm. square. Thirty-six rods of the same preparation are used to form a small open construction by simply superimposing rows of six alternately crossed upon each other, leaving in the center an open space about six cm. wide for the reception of burning material. The whole arrangement is one permitting of the freest possible circulation of air, a condition which is further aided by placing the construction upon a piece of heavy wire gauze, supported upon two bricks. Little bundles of splints, weighing thirty-five grams each, are used as sources of combustion. They are introduced into the central space, lighted, and the result carefully noted. If combustion be not communicated to the construction by the burning of a single charge, a second is added, and so on. It is easily seen from the series of experiments with these constructions carried on before you, that this method of the two Belgian chemists is of the most searching and exacting nature, and yields comparative results of the highest value.

<sup>1</sup> Rapport.

In such a series of tests, for example, a construction of ordinary wood takes fire at the end of one minute, is in complete combustion two minutes later, and at the end of ten minutes leaves a mass of ashes. Wood treated with ammonium chloride takes fire at the end of three minutes and undergoes complete combustion. Wood covered with cyanite takes fire at the end of three minutes and burns slowly for fifteen minutes, leaving the exterior intact. Wood treated with three coats of waterglass stands exposure to four successive charges of combustible, with but little evidence of the propagation of fire, although the surface of the rods is deeply altered by the exudation and swelling of the silicate. Wood treated with ammonium phosphate, or the United Asbestos Co. preparation, is scarcely affected after four successive charges. The construction remains intact with the interior slightly charred.

#### RESULTS THUS FAR ATTAINED.

Leaving the methods of testing, let us now briefly summarize the results of experiment, and experience with fire protectives up to the present date. For textile fabrics, sodium tungstate and magnesium borate yield, unquestionably, the best results, when materials are to be ironed, while ammonium phosphate or sulphate is preferably used in other cases.<sup>1</sup>

The use of the tungstate, especially, is widespread in England. It may be of interest to know that in the laundry of the Queen's palace, all fabrics of vegetable origin are treated with a solution of neutral sodium tungstate of 28° Tw. containing three per cent. of sodium phosphate. This solution is added to the starch also when the latter is employed.

Abel's researches<sup>2</sup> show that in naval warfare, calcium chloride is valuable to protect rope mantelets, while canvas is well protected by stannic oxide and still better by the double silicate of sodium and lead.

The efficacy of sodium tungstate, as well as of the ammonium salts, for the scenery and decoration of theaters, has also been firmly established.

The comparative results of Lochtin's experiments on pure cel-

<sup>1</sup> F. Fischer, *Ding. Poly. Jour.*, 245, 36.

<sup>2</sup> *Amer. Arch.*, 13 and 14.

lulose<sup>1</sup> may well be summarized here as they offer a valuable classification and furnish useful hints; although it must not be forgotten that the tests were elementary in their nature, and the conclusions, hence, open to criticism, as is, in some cases, evident.

Lochtin divides compounds into three classes, with reference to the effects on combustibles. (1) The *antipyrenes*, which render cellulose unflammable when present in relatively small amounts, and when used in weak solutions. (2) *Indifferent substances* which are effective only when present in large amounts. (3) *Substances which favor combustion*.

### I. ANTIPYRENES.

*Quantities of anhydrous substances required to render cellulose unflammable.*

	Minimal strength of solution used in per cent.	Minimal relative weight (cellulose = 100).
NH <sub>4</sub> Cl	1.5	4.2
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.5	4.5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.5	4.5
ZnCl <sub>2</sub>	1.5	4.0
CaCl <sub>2</sub>	1.5	4.5
MgCl <sub>2</sub>	1.5	4.5
Al <sub>2</sub> (OH) <sub>4</sub>	1.5	3.8
KAl(SO <sub>4</sub> ) <sub>2</sub>	2.0	..
ZnSO <sub>4</sub>	1.5	4.5
SnCl <sub>2</sub>	2.5	..
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	1.5	8.5
B <sub>2</sub> O <sub>3</sub>	2.5	10.0

### II. INDIFFERENT SUBSTANCES.

HKO	7.5	..
MgSO <sub>4</sub>	7.5	15
NaCl	7.5	35
Na <sub>2</sub> SiO <sub>3</sub>	17.5	50
SiO <sub>2</sub>	12.5	30
KCl	20.0	45
Na <sub>2</sub> HPO <sub>4</sub>	7.5	30
K <sub>2</sub> HPO <sub>4</sub>	20.0	..
Al <sub>2</sub> 3(B <sub>4</sub> O <sub>7</sub> )	12.5	24
AlPO <sub>4</sub>	10.0	30
Ca <sub>2</sub> 2(PO <sub>4</sub> )	12.5	30
MgHPO <sub>4</sub>	12.5	30
ZnB <sub>4</sub> O <sub>7</sub>	7.5	20
ZnHPO <sub>4</sub>	15+	..
WO <sub>3</sub>	10+	15+
Na <sub>2</sub> WO <sub>4</sub>	10+	15+
(NH <sub>4</sub> ) <sub>2</sub> WO <sub>4</sub>	7.5	10+
Clay (air dry)	..	75
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> and KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	7.5—5	..

<sup>1</sup> Ding. poly. Jour., 290, 230.

## III. SUBSTANCES FAVORING COMBUSTION.

$\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{ZnCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{FeSO}_4$ .

In reviewing the above tables, it is of importance to note that the aluminum hydroxide used is that obtained by double decomposition between sodium aluminate and sodium bicarbonate. The product formed by the action of ammonia on aluminum sulphate is of no value. It will be seen, also, that the somewhat expensive sodium tungstate is much less effective than many other compounds, the chemical nature of which debars them, however, from ordinary application. Thus, (apart from cost), acid or alkaline reaction, difficulty in solution, hygroscopic properties, or readiness to decompose, on contact with hot iron or otherwise, handicap, as it were, most of the antipyrenes. The chief value of Lochtin's work is to be found in the recognition of aluminum hydroxide as so pronounced an antipyrene and the fixing of the conditions under which it is deposited in the most effective form.

The most important and decisive results with regard to the efficiency of the different current protectives of wood are furnished by Boudin and Donny.<sup>1</sup> Using a classification based upon their rigorous and conclusive tests, we can arrange the protectives in the following series, ascending from the least effective to the most effective.

## I. PREPARATIONS OF LITTLE VALUE.

1. Injection of sodium tungstate (56 kgms. per m<sup>2</sup>).
2. " " copper sulphate 20 " "
3. " " calcium chloride 50 " "
4. " of ammonium chloride 48 " "
5. Coating of waterglass (43 per cent. solid residue), 1 coat, 286 grams per m<sup>2</sup>.
6. Coating of waterglass and zinc oxide, 4 coats, 1 kgm. per m<sup>2</sup>.
7. " " Martin's signifuge, No. 4, 2 coats, 450 grams per m<sup>2</sup>.
8. " " Brocher's preparation, 3 "
9. " " Blane's asbestos paint, 2 " 1 kgm. per m<sup>2</sup>.
10. " " cyanite (basic aluminum silicate), 2 coats, 450 grams per m<sup>2</sup>.

<sup>1</sup> Rapport.



II. PREPARATIONS OF SOME VALUE WHICH LESSEN, IN A MARKED DEGREE, THE INFLAMMABILITY OF WOOD.

11. Covering of cyanite, 3 coats, 570 grams per m<sup>2</sup>.
12. " Bell's asbestos paint, 3 coats, 820 grams per m<sup>2</sup>.
13. " waterglass<sup>1</sup> and ferric oxide, 4 coats, 700 grams per m<sup>2</sup>.
14. Covering of waterglass<sup>1</sup> and powdered glass, 6 coats, 900 grams per m<sup>2</sup>.
15. Covering of waterglass<sup>1</sup> (undiluted),<sup>2</sup> 3 coats, 475 grams per m<sup>2</sup>.

III. PREPARATIONS OF THE HIGHEST EFFICIENCY WHICH PREVENT ALMOST ENTIRELY THE PROPAGATION OF FIRE IN WOOD.

16. Covering of the United Asbestos Co. paint (waterglass, sodium aluminate and asbestos), 3 coats, 850 grams per m<sup>2</sup>.
17. Injection of ammonium phosphate, absorption of 75 kgms. per m<sup>3</sup> after boiling for twelve hours in a sixteen per cent. solution of the salt.

These two protectives would seem therefore the high-water mark of what chemists have attained in their efforts to render wood inflammable. With regard to the permanence of their protective power, it has been observed that, after the lapse of two years, wood treated with the asbestos preparation had lost, in no measure, its resistant qualities, while that injected with ammonium phosphate showed an exceedingly slight diminution in the efficiency. No diminution was noticed at the end of nine months in the resistance of injected wood, kept at ordinary temperature, or at 45° C., or covered with a coat of oil-paint. It should be noted also that the solution of ammonium phosphate does not affect nails and other objects in iron even after contact for several months; also that the solutions of the salt must be nearly saturated in order to yield satisfactory results.

Boudin and Donny's experiments would tend to indicate a

<sup>1</sup> In all these tests a waterglass of forty-three per cent. solid residue was used. It was generally diluted with water, but this additional water is not included in the weight per m<sup>2</sup>.

<sup>2</sup> Wood, when first covered with waterglass, presents a varnished appearance. This is not retained long, as the coating soon begins to scale, and the surface is covered with a white efflorescence.

slight lessening in the strength of wood which has been injected. The general conclusions drawn from their investigations are :

1. The incombustibility of wood, *i. e.*, its non-alteration when under the influence of heat, cannot be attained. It is possible, however, to secure its non-inflammability, so as to preserve ordinarily any structure exposed to an accidental fire, or at least to allow time for the arrival of the ordinary extinguishing appliances, unless it be filled with combustible material.

2. Of the preservative processes used, injection of saline solutions or the application of protective coverings, the former would seem ill adapted for timber of large dimensions, but of manifest value for the less bulky forms of wood. In all such cases the use of ammonium phosphate, in saturated solution, offers such incontestable advantages, that, despite its high price, it should be employed unless excluded absolutely by limitations of expense. (Ammonium phosphate can be obtained for about \$50 per 100 kgms., and as a cubic meter of wood absorbs seventy-five kgms., the cost per cubic meter would be about \$38.)

3. In the majority of cases protective coatings are preferable. The most efficacious is that containing sodium aluminate and asbestos in waterglass, while waterglass alone, or with the addition of aluminum hydroxide, is of great value.

#### EXPLANATION OF THE ACTION OF PROTECTIVES.

Such being the practical results attained, it is of interest for us next to know in just what way these chemical compounds act to prevent inflammability. It is, in fact, a matter of surprise that the experimentation in this field has been so largely empirical, neither preceded nor followed by theoretical considerations.

In studying the effects of heat on ordinary wood, the following will be noted:<sup>1</sup> When exposed for some time to a temperature of 200° C., wood becomes light brown and its strength is materially affected. At 300° it is charred completely, losing all power of resistance, but still without a trace of flame. If, however, the wood be in contact with flame, or be exposed to a red heat, change takes place rapidly, and if air have free access it bursts into flame, and combustion does not cease until the entire mass be reduced to ashes.

<sup>1</sup> F. Fischer, *Ding. poly. Jour.*, 245, 36; Boudin et Donny, Rapport.

When wood protected by a suitable coating, such as water-glass, is exposed to a temperature of  $200^{\circ}$  C., it acts exactly as ordinary wood. Wood, however, which has been injected with saline solutions, as ammonium phosphate, is more liable to change. It assumes a deep brown tint, and the resistance to strain is greatly lessened. At  $300^{\circ}$  all forms of protected wood are carbonized, exactly as the ordinary wood, and without flame.

At a red heat, or in contact with flame, prepared wood is completely destroyed; but there is a vast difference between its rate of destruction and that of non-protected wood. At first there is a pronounced period of direct resistance. In cases where external applications have been made, the heat gradually penetrates the protective coating, jets of gas issue through fissures in it, and their combustion contributes to the intensity of the surrounding sources of heat, until, finally, combustion is complete. In the case of wood impregnated with suitable saline solutions, resistance to the flame is likewise marked, but much gas is evolved. This gas is not inflammable but seems, on the contrary, to interfere seriously with the combustion of the surrounding fire. Complete charring is finally reached. It is evident in both cases that the ordinary effects of heat upon wood are seriously hindered or retarded. The first effect of heat, as we have seen, is to produce gas and leave carbon. This gas, if allowed to burn with the oxygen of the air, furnishes a fresh supply of heat to bring about further evolution of gas. But as organic matter and the resultant charcoal are both poor conductors of heat, gasification would proceed very slowly unless the coal on the surface also changed to gas by burning with atmospheric oxygen (as well as by reducing the carbon dioxide and water present), thereby increasing the available temperature. The maintenance of a sufficiently high surrounding temperature must eventually cause the penetration of enough heat into the body of wood exposed to produce complete gasification and carbonization, and finally complete combustion of the charcoal. This action can be retarded evidently by two distinct agencies. The first is the evolution of an inert or non-combustible gas or vapor from the wood through the influence of heat; the second is the presence of an external coating, which is not only a poor

conductor of heat, but also protects the outside zone of charcoal from contact with atmospheric oxygen. It is in one or both directions that fire protectives render service.

The ammonium salts are good types of the first class. Ammonium chloride and ammonium sulphate are readily vaporized and dissociate, the first into ammonia and hydrochloric acid, the second into ammonia, nitrogen, water, ammonium, sulphite, etc. Ammonium phosphate decomposes slowly to metaphosphoric acid (sixty-two per cent. of its weight), ammonia, and nitrogen monoxide. It is probably this slowness of decomposition which renders the phosphate superior to the other ammonium salts. In the case of magnesium chloride, zinc chloride, etc., hydrochloric acid is driven off. In the case of other salts, such as the alums, the borates, copper sulphate, and sodium tungstate, large amounts of water of crystallization are necessarily liberated in the form of aqueous vapor. It is a matter of surprise that this fact, that the storage of considerable amounts of water in the solid form in the interior of wood is a potent factor in the protective value of a number of antipyrenes, should have escaped the attention of chemists. It is an easy matter to calculate the volume of aqueous vapor capable of being formed from a given weight of  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{W}_2\text{O}_7 + 10\text{H}_2\text{O}$  or  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ . There is no question but that such salts, as the above, retard the attack of flame chiefly through this agency at first, although after the expulsion of the water of crystallization, the presence of the saline substance coating the charred surface and acting as a poor conductor of heat, as well as preventing the access of oxygen, continues the protection for a certain time. It is in the varying ability of different compounds to form coherent, continuous protective coatings after exposure to heat that we find the reason of the superiority of one composition, for external application, over another. Thus, waterglass alone gives good results. When wood treated with it is heated, we notice a puffing out and swelling, a certain amount of vapor escapes, and the residue is left as a light, voluminous, fairly coherent covering, through which air can penetrate but slowly to the charred surface beneath, and heat is likewise conducted but slowly. The addition of aluminum

hydroxide to the waterglass seems to increase the resistant properties of this envelope, while the further addition of asbestos and the substitution of sodium aluminate for aluminum hydroxide, forming thereby practically a quadruple silicate of sodium, magnesium, calcium, and aluminum, give the highest resistant power.

It may be pertinently inquired, why does the presence of some salts seem apparently to help combustion? Lochtin explains this action<sup>1</sup> by the uneven distribution of some substances during drying or precipitation, more, proportionately, remaining on the surface of the paper or wood used. Here they form porous but slightly compact crusts; and these favor continued glowing or combustion by preventing a loss of heat.

#### PRACTICAL APPLICATION OF THE KNOWLEDGE GAINED.

With this exposition of the results attained in the contest with fire—the fruit almost exclusively of the work of European chemists—what should be the practical application of the knowledge gained to our own conditions in America? It is evident that there should be a rigorous insistence on the use of protective agencies for *all* wood employed in buildings containing material of permanent value, such as deposits of archives, museums, libraries, etc. Equally rigorous should be the requirement in the construction of exhibition buildings; of churches, theaters, and all structures wherein large assemblages are held; of the stands about our fields for athletic amusements; of cars and craft for transportation by land or water; and above all, of the edifices of our institutions of learning.

The applications enumerated above are nearly all easily within the reach of legislative enactment, as they affect the interests or lives of the public.

How far the use of protective agents may be introduced into ordinary construction, and into household equipment it is difficult to say.<sup>2</sup> In England the custom of protecting wearing apparel of vegetable fiber is widespread. No reason exists why American women, earnest in reform, should not advocate a

<sup>1</sup> *Ding. poly. Jour.*, 290, 230.

<sup>2</sup> *Ding. poly. Jour.*, 245, 36.

similar custom here. There is no question, however, but that great stress should be laid upon the wisdom of impregnating the curtains, draperies, and hangings of our homes.

It is to be hoped that the slow burning principle may soon be extended to domestic architecture, but even with our present methods, it is easily possible with the outlay of a few per cent. on the cost of the house to lessen enormously its fire risk. All beams, joists, studding, etc., which are later to be hidden, can be coated during the process of erection. Siliceous coatings can also be applied to all surfaces outside and inside which are ultimately to be painted. Finally, woods to be used for interior finish can be protected by steeping in a solution, preferably of ammonium phosphate, if not of one of the cheaper antipyrenes, before being varnished. Such a house, if isolated, and presupposing the use of wire lath, is practically fireproof in nineteen out of twenty cases of ordinary conflagration. If provided with brick walls and slate roof, the risk is greatly lessened, and it is not difficult to recognize that blocks or districts of such construction are free from *all* danger of conflagration: that, in fact, fire will be confined exclusively to such rooms or houses as may be used for the storage of combustible material. Insurance, under such conditions, approaches almost the vanishing-point; and the freedom of apprehension from loss by fire is not to be measured by dollars and cents. We are here entering upon the proper province of another science. The chemist has provided the means of coping successfully with the dangers of combustion. It is for the economist to insist on the utilization of his achievements, in assuring increased comfort and security to society. Suffice it only to add that existing structures may, to a great extent, be protected especially for those few precious minutes between the discovery of a fire and the arrival of aid, by the generous application of the siliceous compositions to all exposed woodwork. The direct value of such treatment has been promptly recognized in England by a decrease of fifty per cent. in the insurance rates on houses so treated.

#### FIELD FOR FURTHER INVESTIGATION.

Finally, what remains for the chemist to do in this field?

Indirectly he may accomplish much in lessening the fire risk. First in the study of illuminants. Whatever tends to displace the use of petroleum for domestic lighting tends, by so much, to diminish the national fire bill, as this one substance is a most prolific cause of conflagration. It is to be hoped that the way may be opened to an economical and convenient use in this connection of our vegetable oils, now so abundant; or to the introduction of a fuel-gas saturated with hydrocarbons, so safe and economical that it may be promptly accepted for domestic lighting. The possibilities offered in this direction by the extended utilization of calcium acetylide are also most hopeful. Next there is little doubt but that the early approach of the era of cheap aluminum will effect an important revolution in the use of structural materials, the light, unchangeable metal tending to displace wood in many of its external and internal applications. In this field American chemists have taken the lead.

With regard to the production of new protectives it is hardly probable that the last word has been said. We have seen how experiment, beginning with sodium silicate, led successively to the addition of aluminum hydroxide, of lime, of lead salts, of powdered glass, and of finely divided asbestos to the convenient syrupy medium. There is but little doubt that other combinations, less expensive or more effective than those now in vogue, await the experimenter.

The high rank of aluminum hydroxide among protectives, as shown by Lochtin, should lead to extended research with regard to its availability under different conditions, and its most economical application.

The utility of magnesium borate, so warmly recommended by Patera and Fischer, should be definitely established by comparative tests. It is not unlikely that combinations of the borates and silicates may also be found to render good service. Experiments on the deposition of insoluble tungstate in fabrics are also worthy of being carried out.

With regard to protection, by impregnation, it is doubtful whether any better agency than ammonium phosphate can be

found. It would, however, be advisable to study the economical production of this salt for the purpose in question. Might it not be possible to attain cheapness by using successive baths of ammonium sulphate and sodium phosphate; or could not acid calcium phosphate be brought advantageously into the reaction?

A further field of investigation is the possible combination of injection and painting, impregnation with such deliquescent chlorides, as zinc chloride, or magnesium chloride, being followed by a simple external coat of a siliceous paint. Then the most favorable time for injecting or steeping wood with saline solutions should be definitely ascertained. Is it, after completed seasoning, or when the wood is perfectly green, as advocated by Jones?

The question of the most economical combination of protection against fire and of preservation from decay and insect attack, remains also to be settled.<sup>1</sup> Another important phase is the highest attainable efficiency, from the use of salts which store up, in wood, considerable amounts of water of crystallization, such as gypsum; for it must be borne in mind that every volume of solid water of crystallization yields 1700 volumes of aqueous vapor at 100° C.

It is largely along these lines that we may expect to see advance made in the province whose survey we now complete.

In conclusion, let me express the earnest hope that individually and collectively the influence of this Association may be helpfully thrown in favor of any general effort to lessen our tribute to fire. We have made ourselves felt in movements to combat the twin, although antithetic, evils of drought and flood by the preservation and extension of our forests, as well as in other economic directions. Can we not do the same in availing ourselves of the work of Gay Lussac, Fuchs, Versmann, Oppenheim, Abel, Tessier, Patera, and other chemists, by bringing into the American home and the American community that peaceful security and liberation from a dreaded tax, which comes with the practical abolition of danger from conflagration?

<sup>1</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.



# A STUDY OF THE CHEMICAL BEHAVIOR OF TUNGSTEN AND MOLYBDENUM AND THEIR TRIOXIDES<sup>1</sup>.

BY CHARLES HATCH EHRENFELD.

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## INTRODUCTION.

Group VI of the Periodic System contains a sub-group of more metallic elements—chromium, molybdenum, tungsten, uranium—among the derivatives of which many interesting analogies manifest themselves. Upon comparing the metals themselves, numerous points of interest appear. Thus, beginning with chromium, possessing the lowest atomic mass as well as the highest specific heat, we observe that it oxidizes but slowly when heated in ordinary air. Molybdenum gradually changes under like conditions through its brown and blue oxides until finally it reaches its most stable form, molybdenum trioxide. The same may be remarked of tungsten, although it burns only at elevated temperatures. Uranium, on the contrary, oxidizes at relatively low temperatures. Considering this sub-group as a whole, we can probably detect greater similarities in chemical deportment and analogies in derivatives between molybdenum and tungsten than between the remaining members. To learn more of the behavior of these two metals, to disclose, if possible, differences of conduct while exposed to the influence of the same reagents, is the chief aim of the present investigation. Prefacing the actual study of the metals are some observations upon the deportment of their trioxides which are not devoid of interest, especially as they, in a measure, confirm some earlier observations. The results of this research, while largely of a qualitative character, yet demonstrate quantitative differences between tungsten and molybdenum which serve to define more clearly their position in the Periodic System.

I. *Action of Phosphorus Pentachloride upon Tungsten and Molybdenum Trioxides.*—Persoz and Bloch (*Compt. rend.*, **28**, 86, 389) assert that if the anhydrides of inorganic acids be heated

<sup>1</sup> From author's thesis presented to the Faculty of the Department of Philosophy of the Univ. of Pa. for the degree of Ph.D., 1894.

together with phosphorus pentachloride, the products of the reaction will consist of the anhydride and phosphorus pentachloride. They say, for example, that under this treatment tungsten trioxide yields the derivative  $\text{WO}_3\cdot\text{PCl}_5$ . Hugo Schiff (*Annalen der Chemie*, 102, Heft I) expresses the opinion that in the reaction described, the final products are compounds of equivalent amounts of phosphorus oxychloride with the chlorides of the acids; that tungsten trioxide and phosphorus pentachloride yield a reddish-brown liquid, from which phosphorus oxychloride can readily be distilled, leaving at the same time a reddish-brown residue. The latter, Schiff believes to be tungstyl (or wolframyl) chloride,  $\text{WO}_2\text{Cl}_2$ .

Teclu has made a more recent investigation of this reaction (*Annalen der Chemie*, 187, 255). He finds that as a result of heating tungsten trioxide together with phosphorus pentachloride to  $170^\circ$  in a sealed tube, he obtained tungsten hexachloride. Its solution in phosphorus oxychloride was brown in color.

It seemed to me while engaged in a study of the behavior of tungsten trioxide in vapors of various gaseous compounds, that a repetition of this experiment of Teclu was quite desirable. To this end, equivalent weights of tungsten trioxide and phosphorus pentachloride were intimately mixed, introduced into a porcelain boat, and the latter placed in a hard glass tube contracted at intervals. The air in the tube was expelled by conducting carbon dioxide through it. On applying heat to the boat a white and very volatile crystalline sublimate made its appearance. This was caught at the extreme anterior portion of the tube. Vapors of phosphorus oxychloride were given off, recognizable by their characteristic sharp smell. A brown sublimate next formed beyond the boat. The contents of the boat were reddish-brown in color, melted to a dark red liquid, and gave off reddish-brown vapors resembling those of bromine in color. They condensed to steel-blue colored isometric forms. In every respect they indicated the tungsten hexachloride. A careful examination with a magnifying glass revealed brown needles of the pentachloride distributed around them. These could not be removed, hence the analysis made gave a result that ranges between the theoretical requirements of the penta- and hexa-

chloride. In order to weigh the product and prevent decomposition by contact with air, the tube was sealed at the contracted parts, allowed to cool, and then weighed, after which it was cracked by a hot rod, the contents dissolved out, and the tube refilled with carbon dioxide and reweighed.

0.2562 gram = material.

0.1559 gram =  $\text{WO}_3$  obtained by ignition.

0.1236 gram = W equivalent.

48.25 = per cent. of tungsten obtained.

46.34 = per cent. of tungsten in  $\text{WCl}_6$ .

50.89 = per cent. of tungsten in  $\text{WCl}_6$ .

It may also be observed that the intensity of the heat applied, as well as its duration, had much to do with the quantity of brown material produced. This is not surprising, if the fact be recalled that the hexachloride passes into the pentachloride by ignition in carbon dioxide or hydrogen.

The analysis of another, bright red and more volatile product, showed it to be tungsten oxytetrachloride,  $\text{WOCl}_4$ .

0.0632 gram = material.

0.0423 gram =  $\text{WO}_3$  obtained by ignition.

0.03352 gram = W equivalent.

53.05 = per cent. of tungsten obtained.

53.86 = theoretical per cent. of W in  $\text{WOCl}_4$ .

These experiments were repeated with essentially the same results so that I feel Teclu is justified in asserting that  $\text{rWO}_3 + 5\text{PCl}_5$  give, as direct products, tungsten hexachloride and phosphorus oxychloride. My mode of procedure being somewhat different from that of Teclu will at once explain why in addition to phosphorus oxychloride and tungsten hexachloride, I also got the tungsten pentachloride and oxychloride.

An atmosphere of nitrogen instead of carbon dioxide was tried and gave the same result, but to a less satisfactory degree.

The same method of treatment was also applied to a mixture of equivalent quantities of molybdenum trioxide and phosphorus pentachloride. The reaction took place at lower temperature and was more rapid and energetic than in the case of tungsten trioxide. At first a very volatile white sublimate was deposited in the forward part of the tube, followed by copious brown

vapors. On driving these over gently, a black liquid residue was left in the boat. This solidified, on cooling, forming shining needle crystals which, on examination, proved to be molybdenum pentachloride. Owing to the immediate oxidation in contact with air it was not possible to remove other adhering lower chlorides from the boat, but the latter was at once put into a tube filled with carbon dioxide and thus weighed. The contents of the boat were then dissolved in water and nitric acid and the chlorine determined by titration with tenth normal silver nitrate, potassium chromate being used as an indicator.

0.8296 gram = material.

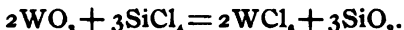
0.51475 gram = chlorine by silver nitrate.

63.25 = per cent. chlorine found.

64.83 = theoretical per cent. Cl in  $\text{MoCl}_5$ .

The low result is accounted for by the presence of lower chlorides which could not be separated.

II. *Action of Silicon Tetrachloride upon the Tungsten and Molybdenum Trioxides.*—Vapors of silicon tetrachloride were passed over tungsten trioxide while the latter was subjected to the heat of a combustion furnace. It was hoped that tungsten hexachloride might be formed according to the equation:



The air was first expelled from the tube by a current of carbon dioxide and then the latter was passed through the small flask containing silicon tetrachloride which was subjected to the heat of a water-bath. No action took place, however, although the operation was continued for about two hours. When a small quantity of air was admitted, tungsten oxytetrachloride and tungstyl chloride were formed.

Silicon tetrachloride was likewise without action on molybdenum trioxide. Rauter (Dissertation, Tübingen, 1893), heated the trioxides together with silicon tetrachloride in sealed tubes. His products were oxychlorides, perhaps in great part due to the presence of air.

III. *Action of Various Gases upon Metallic Tungsten and Molybdenum.* (a) *Action of Nitric Oxide.*—As it was not known whether nitric oxide would have a reducing or oxidizing action it was passed over the metals as well as their trioxides, heat being

applied at the same time. The gas was generated by the action of nitric acid on copper and dried by passing through sulphuric acid. Tungsten trioxide was put into a porcelain boat and the latter into a piece of hard combustion tubing to which heat was applied with one or more Bunsen burners. Nitric oxide gas was passed through the tube and strong heat applied to the boat for half an hour or more. No change was produced on the tungsten trioxide. Molybdenum trioxide treated in a similar way was also unchanged.

Then finely powdered metallic tungsten was placed in the tube, all the air carefully expelled by the current of nitric oxide, and heat applied gradually. At a moderately high temperature (below red heat) action between the metal and nitric oxide began and then proceeded rapidly by means of the heat generated by the reaction, the contents of the boat becoming almost white hot. The product of the reaction was tungsten trioxide.

Metallic molybdenum was subjected to the same treatment. The reaction began only at red heat and proceeded rapidly but with less energy than in the case of tungsten. After continued strong ignition the result of the reaction was not the trioxide but the dioxide of molybdenum.

(b) *Action of Nitrous Oxide.*—Metallic tungsten was placed in the tube and the air carefully driven out of the latter before heat was applied. The action on the tungsten began just as the glass tube began to show signs of redness. The reaction was rapid, with evolution of light and heat, but less energetic than with nitric oxide. Tungsten trioxide was the final product.

Metallic molybdenum, treated in the same manner, required full red heat before any reaction took place. The product was again molybdenum dioxide.

(c) *Action of Nitrogen Peroxide.*—With tungsten, the action began at low temperature, hardly more than  $300^{\circ}$ – $350^{\circ}$ , and proceeded rapidly, but not with the evolution of as much light as with nitric oxide, probably for the reason that the reaction began at lower temperature. Tungsten trioxide was again the product.

With molybdenum the action began at incipient red heat, proceeded with more energy than in the preceding instances, and at once formed molybdenum trioxide.

Considering that nitrous oxide ( $N_2O$ ) shows in its heat of formation ( $-17,740$  Cal.) that it is an endothermic body, and that nitric oxide ( $NO$ ) and nitrogen peroxide ( $NO_2 = -2,045$  Cal.) are members of the same class, it is not surprising that the trioxides of the metals are not in any manner affected by them.

(d) *Action of Sulphur Dioxide.*—Tungsten began to be oxidized at moderately high temperature, but no evolution of light occurred. On continued application of high red heat, only lower tungsten oxides (blue, greenish, and brown) were formed and no trioxide was apparent. A deposit of sulphur was formed on the anterior part of the tube.

With molybdenum, action took place only at the highest temperature, no light being evolved. The oxidation proceeded slowly, and the final product was molybdenum dioxide. Sulphur was deposited on the walls of the tube.

In sulphur dioxide the oxygen is more firmly bound than in any other derivative of these two elements, and yet these metals, molybdenum and tungsten, are capable of withdrawing it.

(e) *Action of Methylamine.*—A current of this gas was generated by heating, in a small flask, a mixture of quicklime and methylamine hydrochloride, the gas being dried by passing over quicklime. The escaping gas was finally conducted into dilute hydrochloric acid. The metals, tungsten and molybdenum, were each heated in this gas. It was thought that a reaction might take place similar to that when metallic potassium is heated in methylamine, namely, the production of the cyanide of the metal. No change, however, took place with the metals, but the dilute hydrochloric acid into which the escaping gas was conducted became charged with hydrocyanic acid. This was undoubtedly produced by the methylamine becoming decomposed in passing through the red hot tube.

IV. *Action of Various Gases on the Tungsten and Molybdenum Trioxides.* (a) *Action of Ethylene.*—Tungsten trioxide heated in a stream of this gas began to be reduced at red heat, the reduction proceeding slowly. Water was condensed on the forward part of the tube, and a mirror of carbon was deposited near the boat. The fact of its being carbon was proved by afterward burning it, no residue being left. After applying heat for about

an hour, a gentle stream of ethylene being maintained, the tungsten trioxide was found to be reduced to a deep blue oxide, quite homogeneous. This oxide was put into an ammoniacal solution of silver nitrate, but after standing more than an hour no metallic silver was precipitated.

Molybdenum trioxide was treated in a similar manner; reduction took place more promptly and readily. A beautiful bronze-brown colored crystalline oxide was left. This was weighed and put into an ammoniacal solution of silver nitrate and digested for some time. The oxide went into solution and metallic silver was precipitated and afterward weighed.

0.0994 gram = weight of material.

0.1538 gram = weight of silver precipitated.

0.0686 gram = corresponding amount of molybdenum,  
according to the proportion :

$2\text{Ag} : \text{Mo} :: 0.1538 : 0.0686.$

69.02 = per cent. Mo in bronze-brown oxide.

70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_5$ .

This result, although not as accurate as could be desired, indicates the brown oxide to be  $\text{Mo}_2\text{O}_5$ .

(b) *Action of Acetylene*.—In a stream of this gas tungsten trioxide was slowly reduced at red heat, a mixture of blue and brown oxides being the result, the latter underlying the former. It may be remarked that in all the reductions and oxidations noticed, the part of the substance near the bottom, or closest to the heat, was most readily acted on, and the reaction most completely carried out.

Molybdenum trioxide was reduced more readily and promptly than tungsten trioxide, and the same bronze-brown oxide was obtained as that from ethylene. Underlying this oxide there was a shining, crystalline, metallic-looking product. In its physical properties it resembled ordinary coke, being light and porous, and easily crushed. A portion of it was put into a silver nitrate solution previously rendered ammoniacal. Metallic silver was precipitated, but there remained black particles undissolved; dilute nitric acid was added and the solution warmed till the silver was dissolved; a black residue was left undissolved. This was filtered out, dried, and ignited on platinum foil; it was completely burned, no ash being left, thus indicating its composition

to be pure carbon. This being the case, it would indicate the probable formation of a *molybdenum carbide*. A quantitative analysis of this material was made as follows: a weighed quantity was put into an ammoniacal silver nitrate solution and gently warmed till metallic silver had separated out. It was then filtered through a weighed filter and dried at  $100^{\circ}$ – $110^{\circ}$ . After weighing, the precipitate was separated, as far as possible, from the filter, and treated with moderately dilute nitric acid and warmed. The silver was dissolved, leaving a black residue of carbon. This was brought upon a dried filter and weighed. Results as follows:

0.1312 gram = weight of "carbide."  
 0.9059 gram = weight of silver and carbon.  
 0.0083 gram = weight of carbon.  
 0.8976 gram = weight of silver by difference.

Calculating the equivalent amount of molybdenum

$6 \text{ Ag} : \text{Mo} :: 0.8976 : x$   
 $x = 0.1329 \text{ gram molybdenum.}$

This gives more molybdenum than the original weight of material, but disregarding this and taking the weights of molybdenum and carbon as found, and dividing by their atomic weights it gives 0.001384 molybdenum to 0.000691 carbon, or two parts molybdenum to one part carbon.

This would indicate a formula,  $\text{Mo}_2\text{C}$ .

Two other analyses were made, only the carbon being determined as above, the molybdenum being taken by difference. Results of second analysis are as follows:

0.0642 gram = weight of "carbide."  
 0.0026 gram = weight of carbon.  


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 0.0616 gram = weight of molybdenum.

These results indicate the formula,  $\text{Mo}_2\text{C}$ .

The third analysis was as follows:

0.1255 gram = weight of "carbide."  
 0.0081 gram = weight of carbon.  


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 0.1174 gram = weight of molybdenum.

This approximates the formula,  $\text{Mo}_2\text{C}$ , as found in the first analysis. It may be that it is not a definite chemical compound but only a mixture, though the yields obtained at different times



for the foregoing analyses had all the same appearance and physical properties. A further investigation of this compound will be made.

(c) *Action of Methane.*—Tungsten trioxide was heated in methane at the highest heat of a Bunsen burner for nearly an hour with no apparent reduction. The full heat of a blast-lamp was then applied which caused the reduction of tungsten trioxide to the blue oxide,  $W_2O_5$ .

Molybdenum trioxide began to be reduced at the ordinary heat of a Bunsen flame. After heating thus to redness for about half an hour the boat was found to contain both metallic molybdenum and the dioxide, the former being underneath the latter.

(d) *Action of Ethane.*—Neither of the trioxides was affected by this gas, though heated for upwards of half an hour.

(e) *Action of Phosphine.*—Tungsten trioxide was first placed in the tube. Reduction began when the flame had been played under the boat only a few times, so that the temperature could not have been above  $125^{\circ}$ – $150^{\circ}$ . Even before any reducing effect was noticed, a faint white vapor rose from the boat but soon disappeared. The reaction proceeded rapidly, leaving a deep-blue colored product in the boat. A sublimate of phosphorus was formed on the sides of the tube. A portion of the blue oxide was weighed off and ignited to the trioxide in order to determine the percentage of tungsten.

0.0563 gram = weight of material.

0.05645 gram =  $WO_3$  obtained by ignition.

0.04477 gram = corresponding weight of W.

79.52 = per cent. tungsten.

This result seems to correspond to the theoretical 79.70 per cent. of tungsten in the oxide  $W_2O_5$ . In another portion of the blue oxide, phosphorus was determined by digesting with nitric acid, thus converting any phosphorus into phosphoric acid, neutralizing with ammonia, and precipitating with "magnesia mixture." The amount of phosphorus found was only between one and two per cent., indicating that it was probably only mechanically admixed with the oxide. A further confirmation of this is the fact that the sides and edges of the boat were observed to be moist after brief standing in air.

Molybdenum trioxide began to show signs of reduction without any application of heat, and when heat was applied in the gentlest way the reduction proceeded rapidly. As in the case of tungsten a faint white vapor was first formed. There was left a beautiful, lustrous, crystalline product with royal-purple color. A yellow film of phosphorus was formed on the sides of the tube. A portion of the purple oxide was ignited to trioxide with the following result:

0.0452 gram=weight of material.  
0.0476 gram= $\text{MoO}_3$  obtained by ignition.  
0.03173 gram=corresponding weight of Mo.  
70.20=per cent. molybdenum.

This corresponds to the theoretical 70.58 per cent. molybdenum in the oxide  $\text{Mo}_2\text{O}_3$ .

Another portion, treated with nitric acid, was completely dissolved; only 1.99 per cent. of phosphorus was found, hence it could not have been chemically combined, but came from phosphorus that had been deposited on the boat.

Ammonia acts upon both tungsten and molybdenum trioxides more energetically, and the products of the reaction are far more complicated than in the above instances. The less basic character of phosphine compared with ammonia explains the difference.

(f) *Action of Arsine*.—The products were the same blue and purple oxides that were obtained with phosphine, but the reduction took place much more sluggishly. As usual, molybdenum trioxide was the more readily reduced. Much metallic arsenic was formed on the sides of the tube. Only a comparatively gentle heat was applied, owing to the ready decomposability of arsine.

A commonly occurring statement made in regard to the hydrides of nitrogen, phosphorus, and arsenic, is that basicity diminishes with rise of atomic mass; hence it is not surprising that arsine should show the sluggish behavior noted above.

V. *Reduction of the Tungsten and Molybdenum Trioxides by Magnesium, Zinc, and Aluminum*.—(a) *Action of Magnesium*.—Tungsten trioxide and powdered magnesium in molecular proportions were mixed and heated in a small glass tube drawn out

to a point. At a low temperature the magnesium was oxidized with a little puff, light being evolved. A gray to black residue was left. This was digested with dilute hydrochloric acid which left a black or slightly grayish residue. A portion of this was weighed off and ignited to tungsten trioxide in order to determine the percentage of tungsten.

0.0858 gram = weight of material.

0.0928 gram =  $WO_3$  obtained by ignition.

0.0736 gram = W corresponding.

85.76 = per cent. tungsten.

This corresponds to the theoretical 85.18 per cent. tungsten in tungsten dioxide, thus showing that the trioxide is reduced to dioxide by magnesium.

The reduction of molybdenum trioxide took place in a similar manner, a black residue being left. This was digested with dilute hydrochloric acid and the molybdenum determined by ignition to the trioxide.

0.0386 gram = weight of material.

0.0466 gram =  $MoO_3$  obtained by ignition.

0.03106 gram = Mo corresponding.

80.48 = per cent. Mo.

This corresponds to the theoretical 80.00 per cent. molybdenum in the sesquioxide, and seems to indicate that magnesium reduces molybdenum trioxide to sesquioxide.

These reductions were also carried out in an atmosphere of hydrogen. At a comparatively low temperature, hardly above  $350^\circ$ , the action between magnesium and tungsten trioxide took place with a little flash of light and the evolution of sufficient heat to crack the combustion tube in which the operation was being performed. The residue was dark gray to black, and looked somewhat metallic. The percentage of tungsten was determined as before.

0.10085 gram = weight of material.

0.1114 gram =  $WO_3$  obtained by ignition.

0.08835 gram = W corresponding.

87.60 = per cent. tungsten.

This seems to indicate the formation of the sesquioxide which contains 88.46 per cent. of tungsten.

Molybdenum trioxide was reduced at even lower temperature,

with formation of the dioxide as shown by the following analysis :

0.1050 gram = weight of material.  
0.1214 gram =  $\text{MoO}_3$  obtained by ignition.  
0.08093 gram = Mo corresponding.  
77.07 = per cent. Mo.  
75.00 = per cent. Mo in  $\text{MoO}_3$ .

The trioxide obtained by ignition was apparently not homogeneous ; this fact taken together with the above variation from the theoretical per cent. makes the above result more than doubtful. Besides, it is hardly likely that a lower oxide would be obtained by reduction in air than in hydrogen.

(b) *Action of Zinc.*—The experiments with metallic zinc were carried out in the same manner as those with magnesium. Heated in air, in a drawn out tube, the mixture of tungsten trioxide and zinc dust began to react at a moderate heat ( $300^\circ$ – $400^\circ$ ), the reduction proceeding slowly throughout the mass without the evolution of light. The residue was a gray to brown mixture, which the estimation of tungsten indicated to be the oxide  $\text{W}_2\text{O}_5$ .

0.1169 gram = weight of material.  
0.12064 gram =  $\text{WO}_3$  obtained by ignition.  
0.09568 gram = W corresponding.  
81.84 = per cent. tungsten.  
82.12 = per cent. W in  $\text{W}_2\text{O}_5$ .

Molybdenum trioxide mixed with zinc dust and heated was reduced more readily and at lower temperature than tungsten trioxide. The action was also more energetic, being concluded with a little explosive puff. Examination of the residue indicated it to be probably  $\text{Mo}_2\text{O}_3$ .

0.1028 gram = weight of material.  
0.1109 gram =  $\text{MoO}_3$  obtained by ignition.  
0.07393 gram = Mo corresponding.  
71.91 = per cent. Mo.  
70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_3$ .

These two experiments with zinc were then repeated in a current of hydrogen. Tungsten trioxide was easily and gradually reduced at about the same temperature as before. The product was brownish ; analysis showed it to be the dioxide.

0.11295 gram = weight of material.  
 0.1202 gram =  $\text{WO}_3$  obtained by ignition.  
 0.09533 gram = W corresponding.  
 84.40 = per cent. tungsten.  
 85.18 = per cent. W in  $\text{WO}_3$ .

Molybdenum trioxide was easily reduced at low temperature, the reaction taking place with a slight puff. The product was brownish in color. Analysis as follows :

0.1070 gram = weight of material.  
 0.1164 gram =  $\text{MoO}_3$  obtained by ignition.  
 0.0776 gram = Mo corresponding.  
 72.52 = per cent. Mo obtained.

70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_5$ ; 75.00 = per cent. Mo in  $\text{MoO}_3$ .

Thus the product seems to be an intermediate one, but this was doubtless caused by impurities. The brownish color of the product suggests, perhaps, that it is the dioxide. If there were an oxide with the composition  $\text{Mo}_2\text{O}_5$ , it would have 72.72 per cent. of molybdenum, which is quite close to the percentage actually obtained.

(c) *Action of Aluminum.*—The trioxides were intimately mixed with molecular quantities of powdered aluminum, placed in a glass tube three or four inches long, sealed at one end, and heated.

With tungsten trioxide there was no action till full red heat was reached when there was a flash and slight report, cracking the tube and scattering its contents. There was not enough material left for analysis, but the walls of the tube were coated with a brownish oxide, probably the dioxide.

With molybdenum trioxide the action was similar, but took place at somewhat lower temperature and was not quite so violent. The sides of the tube were covered with dark blue oxide, probably  $\text{Mo}_2\text{O}_5$ .

These experiments were repeated in an atmosphere of hydrogen but were not successful as no reaction took place. This is undoubtedly for the reason that the temperature required is so high that the trioxides were reduced by the hydrogen before action with aluminum could take place.

At least one interesting fact is brought out by these experiments on oxidation and reduction, and that is that there is a

considerably stronger affinity between tungsten and oxygen than there is between molybdenum and oxygen. This is proved by the fact that in every case the former metal was more readily oxidized while its trioxide was reduced with more difficulty. This is also further illustrated by the experiments with ferric chloride next to be described.

VI. *Reduction of Ferric Chloride by the Metals, Tungsten and Molybdenum.*—A solution of ferric chloride of known strength was made by dissolving piano wire in hydrochloric acid, oxidizing with nitric acid, and evaporating on the water-bath with addition of hydrochloric acid. It was then taken up with water, a few drops of hydrochloric acid added to dissolve basic salts, and the solution, containing 1.11293 grams iron, diluted to one liter.

First a general experiment was made by putting a small indefinite quantity of each metal, in a finely divided state, into an indefinite quantity of ferric chloride solution and a few drops of hydrochloric acid added. The solution containing molybdenum, after standing an hour or so with frequent stirring, lost the yellow color of the ferric salt, hence more was added. The liquid was then largely diluted, a little sulphuric acid added, and a titration made with potassium permanganate to ascertain if reduction of the ferric salt had taken place. A very considerable quantity of ferrous salt was found to be present. The solution containing tungsten stood for several hours but no discharge of color of the ferric salt was noticed. Titration with permanganate however showed a small amount of ferrous salt to be present.

Quantitative experiments were then made to ascertain the relation between the amounts of molybdenum and tungsten and the quantity of ferrous chloride produced. Very small quantities of the metals were taken, as the qualitative experiments showed that the amounts taken for those tests would require a very large amount of ferric solution.

(a) *Molybdenum.*

*First Experiment:*

0.0040 gram = weight of molybdenum taken.

0.01321 gram = metallic iron found by titration.

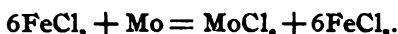
0.01382 gram = metallic iron equivalent to 0.0040 gram Mo.

according to the proportion :

$$\text{Mo} : 6\text{Fe} :: 0.0040 : 0.01382.$$

$$\text{Error} = 0.00061 \text{ gram.}$$

Twenty-five cc. of the ferric solution were used containing 0.02782 gram metallic iron. The molybdenum was completely dissolved. Time of experiment one to two hours. The experiment shows also that 1Mo is equivalent to 6Fe according to the equation,



*Second Experiment :*

0.00445 gram = molybdenum taken.

0.01566 gram = iron found by titration.

0.01557 gram = iron equivalent to 0.00445 gram Mo.

Error = 0.00009 gram.

All the molybdenum was completely dissolved.

Time, one to two hours.

Twenty-five cc. of ferric solution used.

*Third Experiment :*

0.0867 gram = molybdenum taken.

The action with this larger quantity of metal was very slow, and after standing for about forty hours there was still a considerable amount of metal not dissolved.

*Fourth Experiment :*

In this experiment a more concentrated solution of ferric chloride was used containing 11.4022 grams metallic iron to one liter.

0.07857 gram = molybdenum taken.

0.26702 gram = iron found by titration.

0.27499 gram = iron equivalent to 0.07857 gram Mo.

Error = 0.00797.

That is, only 97.10 per cent. of the molybdenum had gone into solution. This solution stood forty-eight hours and there were still small solid particles to be noticed suspended in the solution.

It seems from the foregoing experiments that complete solution and reduction do not take place in a reasonable length of time, except with small quantities of the metal. The results of the first two experiments are interesting as throwing further

light on the valency of molybdenum, and in suggesting an excellent method for the accurate determination of the atomic mass of this metal as compared with iron.

(b) *Tungsten.*

*First Experiment :*

0.0042 gram = tungsten taken.

0.0007345 gram = iron found by titration.

0.00767 gram = iron equivalent to 0.0042 gram tungsten.

according to the proportion :

$W : 6Fe :: 0.0042 : 0.00767$

9.57 = per cent. of tungsten dissolved.

Time, two hours.

*Second Experiment :*

0.00446 gram = tungsten taken,

0.001958 gram = iron found by titration.

0.00814 gram = iron equivalent to 0.00446 gram tungsten.

24.05 = per cent. of tungsten dissolved.

Time, four hours.

*Third Experiment :*

0.00516 gram = tungsten taken.

0.002692 gram = iron found by titration.

0.009422 gram = iron equivalent to 0.00516 gram tungsten.

28.57 = per cent. of tungsten dissolved.

Time, six hours.

*Fourth Experiment :*

0.00475 gram = tungsten taken.

0.005237 gram = iron found by titration.

0.00863 gram = iron equivalent to 0.00475 gram tungsten.

60.69 = per cent. of tungsten dissolved.

Time, eight hours.

These experiments were made with the more concentrated ferric chloride solution. There is seen to be a gradual increase in the amount of iron reduced, roughly proportional to the time ; but complete solution of tungsten could not be obtained, although small portions were allowed to remain over forty-eight hours in the ferric solution.

This reducing power of molybdenum and tungsten, indicated in the preceding experiments, is further corroboration of the



experiments made by Smith (*Ztschr. anorg. Chem.*, 1, 360), with these metals and solutions of silver, gold, and mercury salts. It is further additional comparative evidence of the conduct of the metals of this subdivision of group VI. Of the behavior of chromium in this direction we have no experimental evidence, but of uranium it is known that it reduces salts of tin, platinum, gold, copper, mercury, and silver to the metallic condition. With molybdenum the reduction with these metals proceeds quite rapidly, but the speed diminishes with rise in atomic mass, so that the sluggish action of tungsten in ferric salts is not surprising.

## THE DETERMINATION OF SULPHUR IN PYRITES.

A REPLY TO DR. LUNGE.

BY THOMAS S. GLADDING.

Received March 5, 1895.

IN this JOURNAL (June 1894) I published an investigation of the several methods of estimating sulphur in pyrites. As a result of that investigation I rejected all other methods and recommended, in the strongest terms, the general scheme published by Dr. Lunge in his "Alkali-makers' Handbook." At the same time I advised a few minor modifications as conducive to greater certainty and accuracy. In this JOURNAL (March 1895) Dr. Lunge makes a vigorous attack upon each and every one of these modifications. An examination of his paper brings out the important fact that he admits that every modification proposed is accurate in its nature with one single exception. Unfortunately for Dr. Lunge, the single feature selected for condemnation is the one most easily capable of rigid and positive proof as to its absolute accuracy. I shall reserve the consideration of this point and take up in order the modifications to which such strenuous objection is made.

He objects to the use of one gram instead of half a gram. In reply I have found that by my method one gram is as easily handled as one-half gram and double the accuracy is attained in consequence. He objects to the use of a bromine solution instead of aqua regia as a solvent for pyrites. This substitution was made for the reason that quite often when using aqua regia I was annoyed by the separation of free sulphur. Since adopt-

ing the bromine solution I have *never* experienced this trouble.

His first important objection is against my direction to *always* dissolve the ferric hydroxide and test the same for sulphur. He declares that such procedure is unnecessary. On reading his comments on this point, however, we find that he admits that students in his own laboratory have sometimes failed to get out all the sulphur, through imperfect washing. He further "grants that in important cases the ferric hydroxide ought to be tested in some way or another for any sulphur left behind." If the washing out of *all* the sulphur is so absolutely certain, as he claims elsewhere, why, it may be asked, does he grant what he does? The concession which he makes is a confession of uneasiness of mind on this very point and is all that I could ask for to justify my own instructions. In answer to his criticisms I will simply state that my washing of the precipitated hydroxide was made exactly as he directs. Five or six washings with hot water, "thoroughly churning" up the precipitate each time has never yet, in my hands nor in those of our assistants, completely removed all the sulphur when using one gram. When using one-half gram the danger of losing sulphur would undoubtedly be much lessened, but no careful analyst will neglect the very simple precaution of dissolving the ferric hydroxide in dilute hydrochloric acid and adding ten cc. of barium chloride to the filtrate.

Lunge's second objection is to my addition of the barium chloride solution, one drop per second, to the boiling sulphate solution. He admits that this method is entirely accurate but tedious and unnecessary, taking "about an hour." In reply I will first state that such addition requires only fifteen minutes, and as it is done automatically from a burette, requires no more labor than it does to "pour it in all at once."

But still further I condemn, as inaccurate, Lunge's method of adding the barium chloride all at once. The following comparative tests made, in part, by our assistant Mr. H. E. Cutts and, in part, by myself personally, are very conclusive on this point. A number of samples of pyrites were treated exactly alike in every respect except in the method of adding the barium chloride.

By slow addition. Per cent.	By sudden addition. Per cent.
50.23	50.84
51.00	51.20
51.00	51.32
51.20	51.50
39.13	39.35
39.40	39.90

In the last three samples the filtrates from the ferric hydroxide were divided into two equal portions, and one portion treated in the first manner, the other in the second. Still further tests were made by dissolving two and seven-tenths grams of chemically pure potassium sulphate in 400 cc. of water, adding five cc. of hydrochloric acid and treating as above.

By slow addition.		By sudden addition.
0.4960		0.4990
0.4960	Theory 0.4965	0.5020
		0.5021

I have also taken two grams of chemically pure ammonium sulphate, thus imitating more exactly the conditions of the pyrites analysis as carried out by Lunge and obtained

By slow addition.	By sudden addition.
0.4838 gram sulphur	0.4868
0.4828 " "	0.4900
0.4834 " "	0.4888

Theory calls for 0.4848. The sudden addition of the barium chloride invariably gives results too high.

I quote the following private communication from Prof. Richards, of Harvard College, on this point. "I am much surprised to find that Lunge is ignorant of the occlusion of barium chloride by barium sulphate. This has been known for a number of decades. In 1890 it was so well known to me that I treated it as a matter of course (*Amer. Acad. Proc.*, 26, 258). This year one of my students has finished a comprehensive work upon this subject showing the amount and circumstances of the occlusion. The paper has already gone to press in the *Proceedings of the American Academy* and the *Zischr. anorg. Chem.* It wholly confirms your unpublished statements made to Lunge." This is strong testimony corroborating my results given above. My method of avoiding the occlusion of barium chloride by adding the barium chloride solution *drop by drop* and thus insuring the formation of a chemically pure granular precipitate of barium sul-

phate is the same as that adopted by our National Association of Agricultural Chemists in the precipitation of phosphoric acid as ammonium magnesium phosphate.

The last objection of Lunge refers to my method of estimating the 0.20 to 0.40 per cent. of sulphur that may be left in the ferric hydroxide, by the simple plan of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium chloride solution and letting stand over night. This he declares is decidedly *wrong*.

Here again I will quote from Prof. Richards' letter. "This last paper (Dr. Lunge's) seems to me to contain several errors. I think you will find that *in the presence of a considerable excess of barium chloride*, barium sulphate is *not* very seriously soluble in cold ferric chloride solutions, even when acid (see Jannasch and Richards, *J. prakt. Chem.*, **39**, 328-329). Hence your method is as accurate as most analytical methods.

I wish to call especial attention to the method that Lunge has adopted to support his position on this point. He has taken four samples of pyrites and carried them through a complete analysis by his scheme and also by mine and because his method gives 0.20 per cent. more than mine he concludes that I lose 0.20 per cent. sulphur by the solubility of the barium sulphate in the acid solution of the ferric hydroxide. No such conclusion can be fairly drawn from so unscientific a procedure. A far better plan is to divest the problem of all other possibly interfering errors and strip it down to the naked question in hand. This had been done in my first paper as follows:

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur.....	0.0049 gram.
2. " .....	0.0050 "
3. " .....	0.0051 "

The amount actually present was 0.00496 gram.

I have since repeated the above demonstration by an even more rigid test as follows: I dissolved 0.0135 gram of potassium sulphate in 100 cc. of water, added ten cc. of concentrated

hydrochloric acid, one-half gram of iron, ten cc. of barium chloride solution, precipitating hot and allowing to stand as above. The barium sulphate came down slowly, on cooling. The ignited barium sulphate was snow-white and free from iron, probably on account of its slow formation; I obtained:

1. Sulphur.....	0.0025
2. ".....	0.0026

The amount actually present was 0.00248.

This amount taken in these last experiments corresponds to about 0.20 per cent. sulphur calculated on one gram of pyrites. Lunge claims to have lost this amount on account of the solubility of barium sulphate in acid solution. Were he correct I should have had no precipitate whatever in my experiments above. On the contrary I obtained the whole of the sulphur present to the one-hundredth of a per cent.

To determine sulphur in iron, Troilius, page 38, directs to "dissolve five grams in aqua regia, evaporate to dryness to make silica insoluble. To the filtrate from the silica, which should amount to at least 300. cc., a few cubic centimeters of barium chloride solution are added. After standing one night at the temperature of the room the barium sulphate is completely precipitated." Here we have ten times the amount of iron present that is contained in one gram of pyrites and yet no sulphur is lost. Had Lunge followed the safer and more scientific plan of testing this and also each of the other points in dispute, in the same way that I adopted in my original paper, namely, by working with known amounts of chemically pure salts containing known amounts of sulphur, he would not have fallen into the errors he has.

In conclusion: Of the main modifications proposed by me, Dr. Lunge admits that all are entirely correct, with one exception. The one which he claims to be inaccurate I have incontestably proven to be wholly right. I have also shown that the modification of adding barium chloride, drop by drop, is absolutely necessary to accurate results. I have also shown that the solution of the ferric hydroxide and testing the same for sulphur is certainly the safer course. I conscientiously advise my brother chemists to modify Lunge's method in accordance with my instructions.

## ACIDITY OF GLUCOSE SYRUP AND GRAPE-SUGAR.

BY HORACE E. HORTON.

Received February 18, 1895.

**A**N examination of glucose syrups and grape-sugars will show an acid reaction, and this acidity is due to acid calcium phosphate (rarely), hydrochloric acid, sulphuric acid, and in most instances to sulphurous acid.

The thin liquor obtained by the inversion of starch by acids is strongly acid, and this acidity is reduced by the use of calcium or sodium carbonate to 0.015 gram of hydrochloric acid in 100 grams of liquor.

Acidity due to calcium superphosphate comes from "souring" the bone-black with too strong muriatic acid, when the tricalcium phosphate is broken up with the formation of superphosphate; when a special phosphate black is used in the manufacture of goods, from the occluded superphosphate. I am convinced that in one instance at least, free phosphoric acid had been added to the sample to secure good color.

Sulphurous acid is added to the glucose syrup or grape-sugar when in the cooler.

The acidity is expressed in grams hydrochloric acid or sulphur dioxide in 100 grams substance.

The determination of the acidity was made as follows: 100 grams of glucose or grape-sugar weighed into a beaker and dissolved in about 200 cc. of hot water. A small quantity of carefully prepared delicate litmus solution added, and then titrated with  $\frac{N}{10}$  potassium hydroxide.

I have determined the acidity of a number of American brands with the following results:

CHAS. POPE GLUCOSE CO.

Geneva XXX. 0.0080 sulphur dioxide.

" Jelly 43° Bé. 0.0136 " "

CHICAGO SUGAR REFINING CO.

Confectioners Glucose, 0.012 0.018 0.018 0.018 0.018 0.015 SO<sub>2</sub>.

## AMERICAN GLUCOSE CO.

41° BÉ. Mixing Glucose,	0.0184	0.016	0.019	0.014	SO <sub>2</sub> .
42° " Crystal Glucose,	0.0184	0.0165	0.0205	0.0205	"
43° " Confectioners' Glucose,	0.0184	0.0184	0.0190	0.0184	0.020 "
42° " Brewers' Jelly,	0.0164	0.0164	0.0142	0.0123	"
44° " Export,	0.0172	0.021	0.023		"
42° " Acid Glucose,	0.050	0.048	0.052	0.064	0.0505 "
45° " Export,		0.0225	0.0201		"
"70" Sugar,	0.036	0.032	0.0279	0.021	0.019 HCl.
	0.016	0.018	0.017	0.027	0.028 "
	0.0295	0.0286	0.032	0.040	0.040 "
	0.045	0.0408	0.043		"

WAVERLY FARM, TOPEKA, KAN.,  
February 14, 1895.

## ASH IN GLUCOSE SYRUP AND GRAPE-SUGAR.

BY H. E. HORTON.

Received February 18, 1895.

OF the quantity of ash in glucose syrup and grape-sugar now offered in open market, little is published. Wishing to throw some light on this subject I present figures obtained on analysis of a number of American brands.

The ash determinations were made as follows: Five to ten grams of syrup or sugar weighed in a platinum dish of about 100 cc. capacity, heated with great care until water is expelled, slowly carbonized, and then heated in a muffle at low redness to a finish.

Hydrated grape-sugar, so-called "70" sugar, manufactured by the American Glucose Co.:

Per cent.							
0.536	0.540	0.510	0.510	0.530	0.67	0.31	0.22
0.536	0.540						

Samples of "Special Coloring," American Glucose Co.:

Per cent.		Per cent.
0.31	to	0.52

Samples of "Climax" or "Acme" sugars, manufactured by American Glucose Co.:

"Special dark."	"Dark."	"Light."
0.205	0.16	0.15

"Brewers' sugar," manufactured by Chicago Sugar Refining Co. :

"White." Per cent.	"Standard." Per cent.	"Special dark." Per cent.
0.74	1.00	0.51
0.73	0.72	0.74
	1.15	0.43

"Brewers extract," Chicago Sugar Refining Co., 0.46 per cent.

American Glucose Co., glucose syrups :

	Per cent.		
43° Bé. confectioners' glucose,	0.81	0.33	0.74
41° " mixing glucose,	0.24	0.24	0.26

Chicago Sugar Refining Co. :

	Per cent.		
41° Bé. glucose,	0.14	0.12	0.13
43° " "	1.10	0.65	

National Starch Manufacturing Co., Glen Cove Factory., confectioners' glucose :

Per cent.		
0.80	0.77	0.46

Chas. Pope Glucose., confectioners' glucose, 0.84 per cent.

Peoria Grape-Sugar Works :

41° Bé. glucose,	0.26	0.28	0.26
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The composition of the ash varies with the process of manufacture. If the starch be inverted with muriatic acid and neutralized with sodium carbonate and hydroxide, the ash in finished product will sometimes run over one per cent. and consist almost entirely of sodium chloride.

When oxalic acid is used for inverting and calcium carbonate for neutralizing, calcium oxalate, which is sparingly soluble in glucose solutions, will be found present in glucose, and go over into carbonate on ashing.

When calcium sulphate is used for "brightening" the glucose, a large quantity of it will be present in the ash.

The ash of oxalic acid glucose will contain a small amount of chlorides, coming from muriatic acid used for "souring" the bone, from muriatic added with bisulphite to finished goods in cooler, from sodium chloride by decomposition of calcium chlo-



ride with sodium sulphate after neutralizing, and also from the calcium chloride when the liquor does not receive sufficient sodium sulphate for complete decomposition.

When special prepared phosphate bone is used in the manufacture of syrup and sugar, phosphates are found in the ash. I have found as high as nineteen per cent. of phosphorus pentoxide present.

Iron is present in every ash. It is introduced into the process at the outset and is taken out and as often replaced up to the finish. Batches of glucose made from thin liquor first boiled in a vacuum pan after boiling out with muriatic acid, contain an abnormal amount of iron.

WAVERLY FARM, TOPEKA, KAN.,  
January 20, 1895.

## THE ZIMMERMANN-REINHARDT METHOD FOR THE DETERMINATION OF IRON IN IRON ORES.<sup>1</sup>

BY C. T. MIXER AND H. W. DUBOIS.

Received March 6, 1895.

THE methods chiefly employed in this country for the determination of iron in ores, are the permanganate and Kessler's modification of the old bichromate method (Penny's).

Recently a method has been proposed by R. W. Mahon in the *American Chemical Journal*, 15, 360. The chief feature of this method consists in the proposed use of an indicator solution, for titration with stannous chloride. The indicator solution consists of platinic and mercuric chlorides, the end reaction being indicated by the darkening of the mercurous chloride (formed by the slight excess of stannous chloride), which is caused by the formation of mercurous platinochloride.

As regards this method, it would seem that the frequent standardizations of the stannous chloride that must be made, is a serious objection, and further, the indicator which is used, cannot compare in distinctness with that produced by potassium permanganate.

The objections to the first two methods are mainly those of time consumed in their operation, which specially concerns those who have to make large numbers of determinations. Their general accuracy can hardly be questioned.

<sup>1</sup>This article includes the modifications of the method, as practiced in the Lake Superior iron region.

A preliminary note of the method to be described, appeared in the *Engineering and Mining Journal*, April 14, 1894.

It has been used with most excellent results during the past few years in some of the laboratories on the Lake Superior iron ranges.

The standard works on chemical analysis contain no reference to this method. Furman in his *Manual of Practical Assaying*, page 173, refers rather indifferently to the use of manganous sulphate for titrating in a hydrochloric acid solution with potassium permanganate, but does not seem to be aware of the rapid and accurate method which can be formulated by its use.

Methods have been proposed for titrating directly in a hydrochloric acid solution, but have never proved to be practicable for technical analysis.<sup>1</sup>

The chlorine liberated under such circumstances, seriously affects the results, and it is by the use of manganous sulphate that this is prevented. The use of the above salt for this purpose was first proposed by C. Zimmermann.<sup>2</sup> In this article there is simply outlined the efficacy of manganous sulphate for titrating in hydrochloric acid solutions. Zinc was employed for reduction. A large number of analyses are given, showing the agreement between results obtained from sulphuric acid solutions and hydrochloric acid solutions treated in this manner.

Reinhardt<sup>3</sup> suggested the improvements of reducing with stannous chloride and taking up the excess of the latter, with mercuric chloride, which was then, as now, used in connection with the bichromate method. Later<sup>4</sup> he gives a comprehensive review of the method and suggests a very valuable improvement in the addition of sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid allows the formation of iron phosphate, which being nearly colorless, renders the end reaction more distinct. Otherwise, the presence of the yellow iron chloride will greatly obscure the end reaction.

The solutions required are as follows :

<sup>1</sup> Löwenthal and Lenssen, *Ztschr. anal. Chem.*, 1, 329, and David H. Browne, *J. Anal. Appl. Chem.*, 5, 362.

<sup>2</sup> *Ber. d. chem. Ges.*, 1884 Jahrgang, 15, 779.

<sup>3</sup> Stahl und Eisen, Jahrgang, 4, 704.

<sup>4</sup> *Chem. Ztg.*, Jahrgang, 13, 323. The Journal of the Iron and Steel Institute, 1889, 1, 400, gives a synopsis of this article and an incorrect reference to it.

*Solution A. Stannous Chloride.*—One pound of stannous chloride is dissolved in one pound of hydrochloric acid 1.2 sp. gr., to which water has been added and, when dissolved, is diluted to two liters.

*Solution B. Hydrochloric Acid 1.1 sp. gr.*—Made by mixing equal volumes of acid 1.2 sp. gr. and water.

*Solution C. Mercuric Chloride.*—A saturated solution is made by dissolving in hot water, allowing to cool and crystallize, and then filtering.

*Solution D.*—One hundred and sixty grams of manganous sulphate are dissolved in water and diluted to 1750 cc. with water. To this are added 330 cc.<sup>1</sup> of phosphoric acid (syrup), 1.7 sp. gr., and 320 cc. of sulphuric acid, sp. gr. 1.84.

This solution permits the titration to be made in a hydrochloric acid solution and thus obviates the deleterious action of the chlorine that is liberated by the action of the hydrochloric acid on the potassium permanganate.

*Solution E. Potassium Permanganate.*—Two hundred and fifty grams of potassium permanganate are dissolved in water and diluted to fill an ordinary carboy (about 44 liters). For more accurate determinations, a solution just one-half this strength is used. For the weight we employ, the main solution has the strength, such that one cc. equals two per cent. This solution is standardized by means of an iron ore, the exact value of which has been ascertained in a number of different ways.

*The Standardization.*—For ordinary commercial work, less than one-half gram of the standard ore is taken, the precise weight being so adjusted that one cc. of the potassium permanganate solution is equivalent to two per cent. of iron. Thus, if the standard ore contain 61.20 per cent. of iron, the weight would be so taken, that the reading of the burette would be 30.6 cc. If, however, it should be 30.7 cc., then either the weight would be diminished in the proportion of 30.6 : 30.7, or one-tenth cc. would be subtracted on all subsequent readings of the burette. The latter is the method generally employed when the discrepancy is so slight as this. For the obtaining of the percentage,

<sup>1</sup> Reinhardt recommends a solution more than twice this strength of phosphoric acid, but we have found the above quantity sufficient.

the burette reading is doubled, after making the correction, if such be necessary.

It will be found conducive to accuracy, and require very little extra work, to accompany each series of determinations by a standard ore, which, being under precisely the same conditions, any error in weight or solutions will immediately be detected.

*The Method.*—About one-half gram of ore (exact weight depending, as shown above, upon the standard ore) is placed in a No. 6 lipless beaker, and two and five-tenths cc. of stannous chloride (*Solution A*) added, this being a sufficient amount for ores analyzing between fifty-five and sixty-five per cent. of iron. It is advisable to use a little less for leaner ores. Then ten to fifteen cc. of hydrochloric acid is added (*Solution B*), and, placing a watch-glass on the beaker, the contents are allowed to boil gently on an iron plate until the ore is completely dissolved.

This will generally require only a few minutes, depending mainly on the character of the ore.

When the ore is dissolved, and while the solution is still hot, additional drops of stannous chloride are added from a burette, until all the iron is just reduced to the ferrous state, which is indicated by the disappearance of the greenish-yellow color.

In case a number of ores are being analyzed, it will be found more convenient to bring several of the solutions up to this point and then slightly oxidize them by the addition of a few drops of the potassium permanganate solution.

In case an excess of stannous chloride has been added originally, the solution is also oxidized as above.

The solution, in its slightly oxidized condition, should be kept warm, and the final reduction be made by a drop or two of stannous chloride. It is desirable to have the least possible excess of stannous chloride, after complete reduction has taken place.

During this operation of reduction and oxidation, the solution is constantly agitated by giving the beaker a rotating motion, which alternates in opposite directions.

The final reduction having been made, the sides of the beaker are washed down and five cc. of mercuric chloride (*Solution C*)

added to take up the excess of stannous chloride, which forms a white silky precipitate of mercurous chloride.

After the addition of mercuric chloride, the contents of the beaker are washed immediately into a 500 cc. beaker, in which has been placed six to eight cc. of *Solution D* and about 400 cc. of water. The solution is now ready for titration.

Ores containing organic matter, some magnetites, and pyritous ores, require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow with the regular method. Ores containing small amounts of organic matter, and pyritous ores, are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued.

The use of stannous chloride to hasten the solution of an ore, is particularly convenient in laboratories located in the mining regions. Reinhardt does not mention the use of it. We are not able to state who first proposed its use, but it is not improbable that it may have been accidentally devised independently, by several chemists.

The action of the stannous chloride is doubtless that of converting the iron sesquioxide into the more basic protoxide, towards which the hydrochloric acid asserts a more powerful solvent action.

A tabulation of some results is here given showing the relative rates of dissolving with hydrochloric acid alone, and hydrochloric acid and stannous chloride.

Ore.	No.	Solvent.	Time required for solution.	Iron in Residue.
Soft hematite,	1A	HCl + SnCl <sub>2</sub>	2 min.	0.11
	B	HCl	26 "	0.22
Soft hematite,	2A	HCl + SnCl <sub>2</sub>	4 "	0.09
	B	HCl	35 "	0.12
Specular hematite,	3A	HCl + SnCl <sub>2</sub>	6 "	0.09
	B	HCl	24 "	0.10
Blue granular ore, (Hematite)	4A	HCl + SnCl <sub>2</sub>	6 "	0.18
	B	HCl	30 "	0.21

In order to compare the results afforded by this method with other methods, the following tabulation of analyses has been prepared.

# 410 THE DETERMINATION OF IRON IN IRON ORES.

No.	Chemist.	Location.	Ore.	Method.	Mixer and DuBois Zimmer- mann- Per- Reinhardt	
					cent.	Method.
1	B. E. LaLonde,	Pittsburg and Lake	Lake Angeline			
		Angeline Iron Co.	Hematite.	Bichromate.	63.40	63.40
2	A. G. McKenna,	Edgar Thompson				
		Steel Works.	Pewabic.	"	64.75	64.80
3	A. G. McKenna,	Edgar Thompson				
		Steel Works.	Toledo.	"	41.30	41.20
4	E. P. Jennings,	Ironwood, Mich.		"	61.95	62.05
5	E. R. Brewster,	Iron Mountain,				
		Mich.	Pewabic.	"	63.32	63.38
6	Lerch Bros.,	Virginia, Minn.	Mesabl.	Permanga- nate.	67.44	67.26
7	Porter W. Shimer,	Haston, Pa.	Alabama			
			" fossil ore."	"	48.36	48.25
8	W. E. Hotson,	Iron Mountain, Mich.	Chapin.	Bichromate.	61.87	61.90
9	E. T. Giese,	Mountain Iron,		Zimmermann- Reinhardt.	62.19	62.15
		Minn.	Mesabl.			
9	R. B. Green,	Minnesota Iron Co.,				
		Two Harbors,				
		Minn.	"	"	62.12	62.15
9	C. B. Murray,	Edgar Thompson				
		Steel Works.	"	Bichromate.	62.20	62.15
9	E. P. Jennings,	Ironwood, Mich.	"	"	62.12	62.15
9	Lerch Bros.,	Virginia, Minn.	"	Zimmermann- Reinhardt.	62.12	62.15
9	C. A. Buck,	Bethlehem Iron Co.	"	Permanganate, Jones' Reductor.	62.19	62.15
10	Average of seven chemists,		Lake Superior			
	Illinois Steel Co.	South Chicago, Ill.	Hematite.	All methods.	67.04	67.02
			Salisbury			
			Hematite.	Bichromate.	62.65	62.70
	"	"	"	"	61.74	61.80
	"	"	"	"	61.32	61.30
	"	"	"	"	61.85	61.80
	"	"	"	"	59.27	59.30
	"	"	"	"	61.95	62.00
	"	"	"	"	62.32	62.40
	"	"	"	"	61.62	61.70
	"	"	"	"	62.22	62.30
	"	"	"	"	62.11	62.10
	"	"	"	"	62.15	62.20
	"	"	"	"	62.85	62.80
	"	"	"	"	61.44	61.50

In numbers 1 to 6, inclusive, our figures were based upon the same standard used by the respective chemist, so that the comparison between the methods is rendered independent of any difference due to the standard employed. All the rest of the analyses were based upon our own standard ore, which represents the mean of a large number of determinations, both by ourselves

and other chemists, involving a variety of modes of standardization.

The merits of the Zimmermann-Reinhardt method may be summed up as follows: (a) That the liquid resulting from the solution can be treated directly and without the use of special apparatus. (b) The operation of titration is not tedious as in the bichromate method. (c) That the simplicity of operation permits determinations to be made with rapidity<sup>1</sup> and without sacrifice of accuracy.

The authors desire to express their obligations to Dr. Harry F. Keller, of Philadelphia, Pa., for valuable suggestions made during the preparation of this paper.

LABORATORY OF MIXER AND DUBOIS,  
ISHPEMING, MICH.

## ON THE MANUFACTURE OF SOLUBLE NITROCELLULOSE FOR NITROGELATINE AND PLASTIC DYNAMITES.<sup>2</sup>

J. E. BLOMEN, PH.D.

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THE discovery that a nitrocellulose could be prepared, which was soluble in a mixture of ether and alcohol, other light hydrocarbons, and in nitroglycerol, gave a start to several industries, of which not the least important was that of the manufacture of nitrogelatine, discovered by the Swede, Alfred Nobel. The use of this substance in the production of celluloid, etc., is of great importance to the industries of this country, but falls outside of the scope of this article.

In order that nitrocellulose should be easily soluble in nitroglycerol it ought to be, as nearly as possible, a pure trinitrocellulose. Higher nitration degrees are insoluble in nitroglycerol, a lower one is fully as unsatisfactory in its action and, therefore, the preparation of this substance is considered one of the most difficult problems encountered in the explosive industry. It is, in fact, considered so difficult to produce, that its manufacture is avoided by explosive companies, they preferring to buy the collodion-cotton made for celluloid manufacturing, at a high

<sup>1</sup> In ordinary practice in our laboratory, determinations can be made in five to ten minutes after the ore is weighed out.

<sup>2</sup> Read before the Washington Section, March 14, 1895.

price, in place of running the risk of a failure in manufacturing their own nitrocellulose, although if successful it could be made at a much lower cost.

As a matter of fact, the process of its manufacture is not difficult nor does it require any great chemical skill, but it does require great care in manipulation, uniformity of the materials used, and a never ceasing watchfulness of the details. The cellulose used for its preparation need not be the pure cotton used in the celluloid industry. The inferior article, known in the market as cotton-waste, is quite suitable for this purpose. To be sure the pure cotton is somewhat easier treated and requires less care in the composition of the acids used, but the difference in price between this article and the cotton-waste more than compensates for the additional handling and care. The cotton-waste must, of course, not contain too much fatty matter, but small amounts of organic acids are quite allowable as they are easily removed by suitable washing before using. To do this the bale of cotton-waste is placed in a wooden tank (cedar or best pine wood). I have found that a tank three feet high by five feet in diameter is a convenient size for this purpose. It is now washed, first, with hot water, then with a caustic soda (or sal-soda) solution, about two and one-half pounds caustic soda to a tank full of water, and again thoroughly washed with running hot water. The water having been drawn off, the cotton is taken out and dried, either by hydraulic pressure or by passing it through a centrifugal machine. It is then placed in drying rooms at a temperature of from  $75^{\circ}$  to  $90^{\circ}$  C., for at least two days, or until every particle of moisture is driven out. The next process is to pick the dried cotton into a fine fiber. For this purpose a number of cotton-picking machines are constructed and put on the market. They all possess some merits and are indispensable to a large manufacturing plant for nitrocellulose, but require capital to introduce and skilled labor to run, whereas, on the other hand, "hand-picking" is quite satisfactory, does not require initial capital, and labor otherwise wasted can easily be employed. In trying both machine-picking and hand-picking, I have found that the latter gives a more uniform result, and that (on a smaller scale at least) the time of the men waiting



for the nitration of a previous batch can be profitably used for this purpose.

As is always the case, when a number of nitro-derivatives can be obtained simply by using a stronger or weaker nitric acid and by changing the conditions under which it is used, the tri-nitro-cellulose can be obtained in several different ways. The factors to take into consideration are :

(1) The *proportion* of sulphuric and nitric acids used in the mixture.

(2) The *strength* of the two acids respectively.

(3) The *length of time* the acid mixture is allowed to be in contact with the cotton.

(4) The *temperature* maintained during the reaction.

(5) The *construction* of the plant itself; and a number of minor conditions, such as the humidity of the atmosphere at the time of the reaction.

In addition to this, there is to be taken into consideration in life, outside of the laboratory, such important items as the cheapness of plant, saving of time and economy of labor. To thoroughly investigate and finally bring each one of these conditions into such harmony that the best and most uniform product at the least expense can be produced is, in itself, a life-work and has not so far been accomplished. I will simply indicate the importance of each one of these questions and then describe *one* way, which I have found, after numberless experiments, to give satisfaction; that is, to produce a nitrocellulose soluble in nitroglycerol at a reasonable cost.

If too *much* sulphuric acid be used this is likely to attack the cotton *before* the nitric acid begins to act, converting it partly into cellulose hydrate (this will later be converted into a higher nitration degree by the nitric acid, as it is much more readily acted upon than the cellulose and will then form an insoluble nitrocellulose) and partly into glucose, which will again partly be nitrated to nitrosaccharose, which is insoluble in nitroglycerol and, besides, a very dangerous substance to have present. Again, if too *little* sulphuric acid be present it will soon form its highest hydroxide and be unable to absorb more of the water rapidly formed during the reaction, when the nitric acid will

become diluted and be unable to nitrate the cellulose. The right proportion of acid mixture is, therefore, of great importance.

If *too strong* sulphuric acid be used the result will be the same as above mentioned for an excess of it; if too strong, or too weak nitric acid be used, it is obvious that a higher or lower nitration degree than the one desired will result. It goes without saying, therefore, that the strength of the acids are of utmost importance.

In the reaction between nitric acid and cellulose no fumes are given off, except what is driven off by the heat (in which it widely differs from several other nitration processes) and although the reaction becomes feebler and, eventually, completely stops, when the acid has been diluted to a certain limit, it only gradually diminishes in force, and therefore the time has to be so balanced that the lower nitration degrees have been passed without part of the cellulose having been too highly nitrated, when it is stopped. Hence the importance of careful regulation of the time.

If the nitration pots are surrounded with water kept at a constant temperature, it will be found that the quickness and degree of the nitration depends, to a considerable extent, upon the temperature of this water. Thus, if the temperature be kept up to a high degree the nitration will be much more rapid, but at the same time experience has shown me that, in this way, a *mixture* of different nitration degrees is much more apt to result, than the uniform nitration from one degree to another. Curiously enough, the same result is obtained if no external heat at all be applied, and accordingly in my experience a carefully maintained temperature of 70° C. has been found to give the most uniform result, but no doubt good, and perhaps more economical results can be reached by elevating the temperature of the surrounding water.

It is within the experience of every chemical manufacturer, how much the size and construction of the vessels, in which the reaction takes place, influence the result, and this is fully as true in this industry as in any other. It is especially so as the cotton is so bulky that it is hard to keep every part of it in contact with the acid mixture. Under otherwise the same conditions, I have found quite a difference in the product when it was made on a

clear and dry day, and when the day was rainy or cloudy, the more so, as the building in which the operation takes place has to be left open to a great extent to allow the acid vapors to be carried away.

Even in very large dynamite works it is not always practicable to adopt the very best appliances for the manufacture of nitrocellulose, because it must necessarily be only a small part of the plant, (an average of two per cent. of the ingredients) and can only be conducted by dependence for labor, material, etc., on other parts of the works. In a large plant for the exclusive manufacture of this kind of nitrocellulose the conditions would be more favorable for improvements.

The acid mixture I have found best to use is the following: Nitric acid of 1.430 sp. gr., free from chlorine and such an amount of sulphuric acid as would influence the specific gravity, forty parts; and sixty parts of sulphuric acid of 1.835 sp. gr. The specifications for acids governing the supply for other parts of the works can be adopted for this. It is self-evident that this proportion of acids is only necessary when the work is carried on as hereinafter described and can be greatly varied under different conditions. Such an acid mixture as this cannot be stored in iron drums for any length of time and is therefore troublesome to get, if the nitric acid is not manufactured at the works. The nitric acid must be shipped in carboys; the sulphuric acid can be shipped in drums.

In mixing the two acids a sufficient quantity can be mixed at one time to last for two or three days' supply, and then stored in drums, as the acid will hardly, in this short time, affect the iron to any great extent. The mixing is best effected in a wooden tub lined with heavy lead in such a way as to allow a water-jacket of about two inches around it. (A condemned nitroglycerol apparatus with the coils removed answers this purpose very well.) If compressed air be at hand this should be used as a stirrer by placing a small perforated lead coil at the bottom of the tank and letting the air bubble through the mass since it is very difficult to get any other kind of stirrer that will stand the acids. The men should be warned to have the earthen-ware faucet at the bottom of the tank well greased, to tap it very

gently, to always use their rubber gloves and to have an ample supply of water close at hand.

This mixture although carefully made from acids of 1.430 and 1.835 sp. gr. respectively, will vary in specific gravity from 1.678 to 1.682, but if below or above this, some mistake has been made in the mixing or stirring. The nitric acid should always be dumped in the tank first and the sulphuric acid afterwards so as to give the latter a chance to mix by gravity as much as possible. Just before using, the acid mixture should be stirred again. For this purpose it is convenient to have a lead-lined tank, with an air-stirrer, of a size to hold one charge for the nitrating pots in use, in which the mixture is stirred up thoroughly and then drawn off for each pot as rapidly as possible.

The arrangement of the nitration pots, of course, must depend on existing conditions, such as size and form of the building, the size of the pots, the material used for confining the water around them, the supply of water of suitable temperature, etc. Under ordinary circumstances I have found it practicable to use earthenware pots sixteen inches deep and thirteen inches in diameter, enclosed in wooden troughs twenty feet long by twenty inches wide, connected by means of leaden pipes. If shorter it is a waste of lumber, if longer they are likely to leak from the pressure. If the troughs can conveniently be made from concrete or brickwork with water-tight mortar, of course it can be extended to any desired length.

Experience has shown two pounds to be the right amount of cotton to be used in one nitration pot. To save time and labor it is important to nitrate as much as possible at one time, but the necessity of getting a uniform product limits the amount, and as the cotton clogs or packs together as soon as wet by the acid mixture, only so much can be used at one time as will allow the mixture to act uniformly on the whole bulk of the cotton, without nitrating the outer portion too much and the inner portion too little. After having tried different amounts I have reached the conclusion that (under the given conditions) two pounds is the maximum that can safely be treated in one nitration pot.

Forty-five pounds of the well-stirred acid mixture is weighed

out and placed in the pots, which are surrounded by water heated to  $70^{\circ}$  C. The two pounds of cotton for each pot should be previously weighed out, and ready to be put in so as to have this done as nearly simultaneously as possible. It is now immersed in the acid mixture, turned about a few times with a fork and kept down by a perforated cover. The only reason for using such an excess of acids is that the cotton must be covered by it—if good covers are used forty pounds or less is enough. Besides the perforated covers, each pot should be provided with solid overlapping covers to keep back the fumes. It is now left for one hour and ten minutes, except that after thirty-five minutes the cotton is quickly turned about with the fork, a couple of times and the covers replaced. After this the nitrated cotton is quickly taken up, squeezed with the fork, and wrung out in a centrifugal machine. From this it is taken to a large-sized tank well filled with cold water, where it is thoroughly washed. It should be kept in this tank in running water for about one hour. It is well to have a large quantity of water to prevent heating by adherent sulphuric acid, but it is not so important as in the case of guncotton, because it is not so easily ignited by the heat generated nor is the acid as strong as in the latter case. It is then transferred to another tank of the same size. This is conveniently placed below and the nitrocellulose transferred on a wooden slide. Here it is washed in a sal-soda solution. From this it is taken to a pulping machine or hollender, where it is reduced to a fine pulp. This part of the process is of the greatest importance as it has been proven time and time again that if insufficiently pulped it is hard if not impossible to dissolve it in nitroglycerol. I have found that nitrocellulose, which had before been rejected as insoluble, worked very well after it had passed two or more hours in the pulp-machine. From the pulp-machine it is emptied into a large tank, allowed to settle, and the water filtered off. It is then passed either through a centrifugal machine or a hydraulic press, and thus freed from water as far as possible. It is spread in drying boxes to a depth of about two inches and kept at a temperature of about  $80^{\circ}$  C. till thoroughly dried. After that it is rubbed through fine screens until as fine as the finest flour. If treated in this way the nitrocellu-

lose will dissolve very quickly in nitroglycerol. Seven per cent. of nitrocellulose dissolves in ninety-three per cent. nitroglycerol in less than twenty minutes to a transparent jelly and three and five-tenths per cent. gives the nitroglycerol the consistency of syrup. Several hundred analyses of nitrocellulose prepared in this way show it to contain from 20.5 to 21.8 per cent. of  $\text{NO}_2$ , which very nearly corresponds to the formula of trinitrocellulose. The process carried out in this way is simple and requires no great skill or experience. The cost under ordinary circumstances and with conscientious supervision varies between thirty-five to forty cents a pound. The spent acid must of course be taken care of either by regaining it or by using it direct for other chemical processes. The only laboratory facilities that are absolutely needed are three different hydrometers, one thermometer, and a specific gravity jar—provided the acid contractors are honest.

If the nitric acid be made at the works there is no difficulty in economizing by using the lower grades made up to strength, from the acid for nitroglycerol manufacture, for instance, or from other high grades. If properly and constantly tested the waste nitroglycerol acids can be made up to strength if sufficiently strong nitric and sulphuric acids are on hand. A good and attentive chemist is certain to be able to use the products from other parts of the works (nitroglycerol works, regaining works, acid works, etc.), in such a way as to accomplish a considerable saving in the price above quoted of nitrocellulose. The conditions and facilities for making it differ, but it is safe to say that the makers can save from ten to twenty-five per cent. of the cost of manufacture in the above way by the employment of a competent chemist, to say nothing of what they save by not buying the collodion-cotton of the market at \$1.00 a pound.

The best way to test the nitrocellulose for efficiency in the laboratory is undoubtedly by trying its solubility in nitroglycerol under the same conditions as prevail in the works, next to that is to note the time and result in dissolving it in an ether-alcohol mixture, and finally to use Lunge's nitrometer. The last test, though of less direct practical value, will enable the chemist to obtain a pretty good idea of what he is making and a well-

kept record of all these tests is sure to soon make it possible to always turn out a uniform product—the great desideratum in all chemical industries. The laboratory method of testing, and analysis of materials for, and products of this industry are so simple that they need not be mentioned to an assembly of chemists.

COLUMBIAN UNIVERSITY, February, 1895.

### NEW BOOKS.

**ELEMENTS OF QUALITATIVE AND QUANTITATIVE CHEMICAL ANALYSIS.**  
By G. C. Caldwell, B.S., Ph.D. Third Edition, Revised and Enlarged.  
pp. 187. Philadelphia: P. Blakiston, Son & Co. Price, \$1.50.

Dr. Caldwell has made several changes in this third edition which increases the value of a book which already had much to recommend it, as the writer can testify, having used it in the laboratory for two years. Nitroso  $\beta$ -naphthol is added as an additional test for nickel and cobalt. It would seem as though more tests might be added for the basigens, with advantage to the student. On page 15, the equation for the oxidation of oxalic acid by potassium permanganate is not correct in this, as it was not in the former edition. The marks  $\sim$ ,  $\sim$ , to indicate respectively "precipitate" and "gaseous product," so far as we know entirely original with the author, are great aids to the instructor in the class-room drills. The discussions in Part I on the processes of analytical chemistry are particularly valuable, while the preliminary discussions preceding the schemes, on "the chemistry of the work" are an excellent feature. Lawrence Smith's method for alkalies is added in this edition. While the portion devoted to quantitative analysis is necessarily abbreviated in a work of this character, sufficient space is given to allow students of limited time to get a very good general knowledge of the methods employed. But we would like to have seen the determination of potash added to those of phosphorus pentoxide and nitrogen, for those interested in agricultural analysis.

ALBERT H. WELLES.

**ELEMENTARY QUALITATIVE CHEMICAL ANALYSIS.** By FRANK CLOWES, D. Sc. LOND., AND J. BERNARD COLEMAN. pp. 180. Philadelphia: P. Blakiston, Son & Co. Price \$1.00.

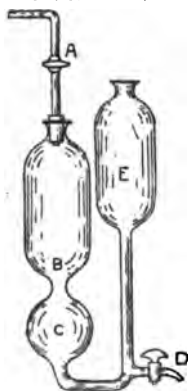
The reviewer fails to discover any important improvements in the arrangement or matter in this book upon others of the same

class. A good deal of space is devoted to directions for manipulation, preparation, and preservation of apparatus. Part of it is given to simple experiments usually included in other books than one intended for qualitative analysis. The methods for working with the blowpipe are far from being full. The tables are the same as ordinarily seen in books on qualitative analysis and present no feature for especial comment. The clumsy terms *mercurosum* and *mercuricum* are employed. Needless and misleading abbreviations, as  $\overline{H\bar{A}}$  for  $C_2H_2O$ , are used. The neatly bound book has a good index and is well printed.

CHAS. BASKERVILLE.

### NOTES.

*A New Hydrogen Sulphide Generator.*—The accompanying figure shows a hydrogen sulphide apparatus in which objectionable features are reduced to a minimum, and the greatest convenience secured. At B is a perforated disk of lead, glass, or porcelain which supports the ferrous sulphide. When the stop-cock at A is closed, the acid is forced back by the gas into the vessel E. The globe C receives the excess of gas and prevents its bubbling back into E. When the acid is exhausted, it is drawn off at D and a new supply is added above.



The advantages of the apparatus are as follows :

1. It is in one piece.
2. The pressure is small when the cock is closed.
3. The quantity of escaping gas is reduced to a minimum.
4. It is conveniently filled and emptied.
5. It is always ready.

The apparatus is attached to a suitable support. It may be made of any size. The one now in use in the laboratory of Cumberland University has vessels and globe eight centimeters in diameter. It was made for me by Messrs. Eimer and Amend, New York, and is giving entire satisfaction.

CUMBERLAND UNIVERSITY,  
LEBANON, TENN.

J. I. D. HINDS.



*Molybdenum Carbide.*—Under date of April 4th, Mr. C. H. Ehrenfeld sends the following additional information upon the supposed molybdenum carbide (see page 388 of this issue):

"Further investigation of the supposed molybdenum carbide has shown that it is undoubtedly only a mechanical mixture. Analyses of different yields of material gave no concordant results. The amount of carbon present seems to depend very largely upon the conditions under which the compound is obtained. For example, when the operation is conducted slowly, at the comparatively low temperature of a Bunsen burner, the percentage of carbon is much greater than when the material is obtained by using the high heat of a blast-lamp."

*The Gas contained in Uraninite* is, according to Profs. Ramsay and Crookes (*Chem. News*, 71, 151), a mixture of helium and argon with a little nitrogen. Prof. Crookes' measurements of the helium line give, as the wave-length, 587.45, while according to Angstrom the wave-length of the helium line is 587.49, and according to Cornu 587.46. In this connection the following extract from Hillebrand's paper describing the occurrence of nitrogen in uraninite is of interest (*Am. J. Sci.*, [3], 40, 384).

"The nitrogen is set free from the mineral as nitrogen gas by the action of a non-oxidizing inorganic acid, and by fusion with an alkaline carbonate and probably also caustic alkalies in a current of CO<sub>2</sub>. As obtained by the use of acids the gas is colorless, odorless, a non-supporter of combustion, unchanged by mixture with air, neutral to litmus papers, not absorbed by caustic alkalies, and insoluble in water, at least its coefficient of absorption is so small as to be inappreciable without elaborate experimentation. When subjected in a eudiometer to the ordeal described by Bunsen<sup>1</sup> there results no alteration in volume, other than that caused by the union of the hydrogen and oxygen added.

This evidence, while fairly conclusive as to the nature of the gas, was purely negative, and proof of a more positive character was sought. Nitric acid is formed from a moist mixture of the gas with pure oxygen by long continued passage of the electric spark, and ammonia is produced by the so-called silent discharge

<sup>1</sup> Gasometrische Methoden, 2d ed., pp. 73 and 74.

through a mixture of the gas with three volumes of electrolytic hydrogen. The contraction produced in the latter case could be measured by cubic centimeters, and water used as an absorbent of the ammonia colored red litmus paper deep blue, besides giving a strong ammonia reaction with Nessler's reagent. With dilute hydrochloric acid as an absorbent there was obtained an abundant precipitate of ammonium platinic chloride. In a Geissler tube under a pressure of  $10^{\text{mm}}$  and less the gas afforded the fluted spectrum of nitrogen with great brilliancy." \* \*

"Throughout the whole list of analyses in which nitrogen has been estimated the most striking feature is the apparent relation between it and the  $\text{UO}_2$ . This is especially marked in the table of Norwegian uraninites recalculated, from which the rule might almost be formulated that; given either nitrogen or  $\text{UO}_2$ , the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the  $\text{UO}_2$ , the higher likewise is the nitrogen."

*Compounds of Argon.*—Berthelot finds that argon combines with the vapor of benzene under the influence of the silent electric discharge giving a yellow resinous odorous substance condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, when heated, is decomposed, leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus blue, indicating that an alkaline substance is contained in them. (From a translation of Berthelot's article in the *Chem. News*, 71, 151.)

**ERRATA.**—In Professor Venable's article in the February number the name of Victor Meyer occurs in several places. It should read Lothar Meyer.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### GERHARD KRÜSS.

Received April 4, 1895.

THE death of Professor Krüss at the early age of thirty-five, and in the midst of a career already remarkably brilliant and fruitful, will be keenly felt by all, and especially by those who have known him as teacher and friend.

He was born at Hamburg on the 14th of December, 1859, his father being the well-known optician A. Krüss. In 1879 he went to the University of Munich and entered upon the study of chemistry with Baeyer and Zimmermann as his teachers. The summer semester of 1881 he spent at Heidelberg studying under Bunsen.

His early acquaintance with physical instruments, and especially with the spectroscope, led Krüss to a series of investigations, begun while he was yet a student, in the field of spectroscopic chemical analysis. In his first paper, which appeared in 1882, he described a method for ascertaining, by means of the spectroscope, whether two colored solutions, when mixed, act chemically upon each other or exist together unchanged. Pursuing this question still further he obtained the interesting results which are recorded in the series of articles upon "The relation between the composition of organic compounds and their absorption spectra," wherein he proved by many measurements of the absorption bands of indigo and fluorescein and their derivatives that the introduction of methyl, oxymethyl, ethyl, or bromine in the place of an atom of hydrogen moved the absorption in the spectrum towards the red, while the introduction of a nitro

or amido group had the opposite effect. Krüss saw and clearly described the practical bearing of these discoveries, and as a result the spectroscope is now employed at Höchst, both for the examination of the purity of known dyes and as a guide to the production of new ones.

Krüss was also greatly interested in the application of the spectroscope to quantitative determinations, his researches upon this subject being largely recorded in the book which he and his brother, Hugo Krüss, published in 1891—*Kolorimetrie und Quantitative Spektral-analyse*. In 1892 appeared his book upon the use of physical methods in chemistry, entitled *Spezielle Methoden der Analyse*.

Krüss's first strictly chemical researches were taken up under the able guidance of Clemens Zimmermann, at whose suggestion he undertook the investigation of the sulphur compounds of molybdenum, thus continuing the studies in the chromium group which Zimmermann had so brilliantly begun by his researches upon uranium.

After the death of Zimmermann (March, 1885) Krüss turned his attention to the study of the compounds of gold. In these investigations, which extended from 1886 to 1893, he corrected the older statements concerning the gold oxides, showing that only  $\text{Au}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{Au}_2\text{O}_4$  exist, redetermined the atomic weight of the element, measured the spark spectrum given by a neutral solution of gold chloride, and, partly in connection with his students, investigated the compounds of gold with the halogens and with sulphur.

In 1886 he became Privatdocent at Munich, and in the following winter, 1886–7, he visited Nilson in Stockholm, beginning, under the guidance of that eminent investigator, his study of the rare earths. The remarkable industry with which they prosecuted their mutual researches is evidenced by the number and importance of the contributions appearing under their names in the *Berichte* for 1887.

The wide reputation which Krüss had thus so early won attracted to Munich many enthusiastic workers in the domain of inorganic chemistry, and the obtaining of a place in his private laboratory was a privilege that was eagerly sought. Upon those

who had the good fortune to work under his immediate direction the attraction exerted by his ability and wide and accurate learning was quite equaled by the charming personality of the man. Quiet and unassuming in manner, and never prone to dogmatic direction of the work in hand, he yet gave to each piece of research a critical attention and kindly and suggestive criticism that was wonderfully helpful and inspiring. Although he could scarcely be called either a graceful or a fluent lecturer, he possessed to an unusual degree originality and clearness in exposition. In May, 1890, he was advanced to the professorship of analytical and special inorganic chemistry in the University of Munich, and this position he held at the time of his death.

The latter part of Krüss's work lay chiefly in the obscure and difficult field of the rare earths, and while these researches are too numerous to admit of detailed mention here, a glance at the mere titles will suffice to show their variety and extent. Besides critically studying the characteristics of many of the different "earths," he greatly developed the methods of separation and examination of these allied elements. Among the many other admirable papers which appeared in the meantime there may be mentioned that with Moraht upon glucinum, with Ohnmais upon the sulpho-salts of vanadium, and with Thiele upon the condition of iodine in solution and the probable cause of the differences in color of its solutions.

The services of Professor Krüss to inorganic chemistry were still further increased by his founding in 1892 the *Zeitschrift für anorganische Chemie*, a journal which he edited with great skill and success. It met with very favorable reception from the beginning, and in the short space of three years it has fully attained what Krüss stated in his introduction to the first volume to be its goal—"to materially advance the development of inorganic chemistry."

The illness to which Krüss finally succumbed began as far back as last October, but in spite of bodily suffering he resolutely continued his lectures and instruction at the laboratory. With the new year, however, his strength began to fail and, gradually sinking, he finally passed away early on the morning of the third of February.

To those who knew Krüss and his work there will recur, as

aptly characterizing him, the words of Berzelius about Liebig—"The man unites, to an unusual degree, unassuming amiability with extraordinary industry and rare scientific ability."

L. M. DENNIS.

PUBLISHED RESEARCHES OF PROFESSOR KRÜSS.

- 1882. Ueber die Constitution von Lösungen, Ber. d. chem. Ges., 15, 1243.
- 1883. Ueber die Schwefelverbindungen des Molybdäns, Ber. d. chem. Ges., 16, 2044.
- 1883. With S. Oeconomides: Beziehungen zwischen der Zusammensetzung und den Absorptionsspektren organischer Verbindungen, Ber. d. chem. Ges., 16, 2051.
- 1883. Ueber die Schwefelverbindungen des Molybdäns, Ann. Chem. (Liebig), 225, 1.
- 1884. Ueber eine neue Darstellungsmethode für Nitrile, Ber. d. chem. Ges., 17, 1766.
- 1884. Ueber die Schwefelverbindungen des Molybdäns, Ber. d. chem. Ges., 17, 1769.
- 1884. Einige Beobachtungen über die höheren Sauerstoffverbindungen des Kupfers, Ber. d. chem. Ges., 17, 2593.
- 1884. Ueber den Einfluss der Temperatur auf spektralanalytische Beobachtungen und Messungen, Ber. d. chem. Ges., 17, 2732.
- 1885. Zur quantitativen Spectralanalyse, Ber. d. chem. Ges., 18, 983.
- 1885. Beziehungen zwischen der Zusammensetzung und den Absorptionsspektren organischer Verbindungen, Ber. d. chem. Ges., 18, 1426.
- 1885. Titerstellung der Lösungen von Kaliumpermanganat, Ber. d. chem. Ges., 18, 1580.
- 1885. Ueber innere Molekularbewegung, Ber. d. chem. Ges., 18, 2586.
- 1886. Ueber die Oxyde des Goldes, Ber. d. chem. Ges., 19, 2541.
- 1886. Ueber die Reducirbarkeit der anorganischen Sulfosalze durch Wasserstoff, Ber. d. chem. Ges., 19, 2729.
- 1886. Ueber einen Universalspectralapparat für qualitative und quantitative chemische Analyse, Ber. d. chem. Ges., 19, 2739.
- 1886. Untersuchungen über das Gold, (First Paper) Ann. Chem. (Liebig), 237, 274.
- 1887. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 20, 205.
- 1887. Ueber sublimirtes Aurichlorid, Ber. d. chem. Ges., 20, 211.
- 1887. Untersuchungen über das Gold, (Second Paper) Ann. Chem. (Liebig), 238, 30 and 241.
- 1887. With L. F. Nilson: Ueber das Aequivalent und Atomgewicht des Thoriums, Ber. d. chem. Ges., 20, 1665.
- 1887. With L. F. Nilson: Ueber die Erden und die Niobsäure des Fergusonites, Ber. d. chem. Ges., 20, 1676.
- 1887. With L. F. Nilson: Ueber das Product der Reduction von Niobfluorkalium mit Natrium, Ber. d. chem. Ges., 20, 1691.
- 1887. With L. F. Nilson: Ueber Kaliumgermanfluorid, Ber. d. chem. Ges., 20, 1696.

1887. With L. F. Nilson: Studien über die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 20, 2134.
1887. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 20, 2365.
1887. With Ludwig Hoffmann: Ueber die Sulfide des Goldes, (First Paper), Ber. d. chem. Ges., 20, 2369.
1887. With F. W. Schmidt: Beiträge zur Kenntniss der Goldhalogenverbindungen, Ber. d. chem. Ges., 20, 2634.
1887. With Ludwig Hoffmann: Ueber die Sulfide des Goldes (Second Paper), Ber. d. chem. Ges., 20, 2704.
1887. With L. F. Nilson: Die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 20, 3067.
1887. With L. F. Nilson: Ueber die Dampfdichte des Thoriumchlorids, Ztschr. phys. Chem., 1, 301.
1887. With L. F. Nilson: Ueber die spezifische Wärme des Niobwasserstoffs und der Niobsäure, Ztschr. phys. Chem., 1, 391.
1888. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 21, 126.
1888. Ueber ein neues Vorkommen des Germaniums, Ber. d. chem. Ges., 21, 131.
1888. With L. F. Nilson: Die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 21, 585.
1888. Beziehungen zwischen Zusammensetzung und Absorptionsspectrum organischer Verbindungen, Ztschr. phys. Chem., 2, 312.
1888. With Paul Kiesewetter: Beiträge zur Kenntniss der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 21, 2310.
1888. With Erich Jäger: Zur volumetrischen Bestimmung der Kohlensäure in Carbonaten, Ztschr. anal. Chem., 27, 721.
1888. With F. W. Schmidt: Beiträge zur Kenntniss der Goldhalogenverbindungen, J. prakt. Chem., 38, 77.
1889. With F. W. Schmidt: Untersuchung über das Kobalt und Nickel, Ber. d. chem. Ges., 22, 11.
1889. With F. W. Schmidt: Untersuchung über Kobalt und Nickel, Notiz. Ber. d. chem. Ges., 22, 2026.
1889. With Erich Jäger: Untersuchung über das Chrom, Ber. d. chem. Ges., 22, 2028.
1889. With Hermann Moraht: Zur spectrocolumetrischen Eisen- bzw. Rhodan-Bestimmung, Ber. d. chem. Ges., 22, 2054.
1889. With Hermann Moraht: Ueber Eisendoppelpseudorhodanide, Ber. d. chem. Ges., 22, 2061.
1889. With Max Althausse: Beziehungen zwischen Zusammensetzung und Absorptionsspectrum organischer Verbindungen, Ber. d. chem. Ges., 22, 2065.
1890. With Hermann Moraht: Untersuchungen über das Beryllium, Ber. d. chem. Ges., 23, 727 and 2552.
1890. With Karl Ohnmais: Ueber Vanadinsulfosalze, Ber. d. chem. Ges., 23, 2547.
1890. With Hermann Moraht: Untersuchung über das Beryllium (First Paper), Ann. Chem. (Liebig), 260, 161.

1890. With Hermann Moraht: Ueber die Reaction zwischen Ferrisalzen und löslichen Rhodaniden, Ann. Chem. (Liebig), 260, 193.

1890. With Hermann Moraht: Untersuchung über das Beryllium (Second Paper), Ann. Chem. (Liebig), 262, 38.

1890. With Karl Ohnmais: Ueber Sulfosalze des Vanadins, Ann. Chem. (Liebig), 263, 39.

1891. Beiträge zur Chemie des Erbiums und Didyms, Ann. Chem. (Liebig), 265, 1.

1892. With H. Krüss: Beiträge zur quantitativen Spektralanalyse, Ztschr. anorg. Chem., 1, 104.

1892. With Hermann Moraht: Ueber die Reaktion zwischen Ferrisalzen und löslichen Rhodaniden, Ztschr. anorg. Chem., 1, 399.

1892. With F. W. Schmidt: Atomgewichtsbestimmungen von Nickel, Ztschr. anorg. Chem., 2, 235.

1892. Einige Bemerkungen über die Untersuchung der seltenen Gadoliniterden, im besonderen über die Aequivalentbestimmung dieser Erden durch Ueberführung von Oxyd in Sulfat, Ztschr. anorg. Chem., 3, 44.

1892. Elektrolyse von Lösungen seltener Erden, Ztschr. anorg. Chem., 3, 60.

1893. With K. Hofmann: Einwirkung von Kohle auf Salzlösungen seltener Erden, Ztschr. anorg. Chem., 3, 89.

1893. With A. Loose: Verhalten der Gadoliniterden gegen Kaliumchromat, Ztschr. anorg. Chem., 3, 92.

1893. Verhalten der Gadoliniterden gegen Anilin und gegen salzsaures Anilin, Ztschr. anorg. Chem., 3, 108.

1893. Ueber die Bildung von Sulfosalzen des Vanadins, Ztschr. anorg. Chem., 3, 264.

1893. Ueber die Erbinerde, Ztschr. anorg. Chem., 3, 353.

1893. With F. W. Schmidt: Ueber die Doppelhalogenverbindungen des Goldes, J. prakt. Chem., 47, 301.

1893. With K. Hofmann: Ueber die Holminerde, Ztschr. anorg. Chem., 3, 407.

1893. With F. W. Schmidt: Ueber die Einwirkung von Chlor und Brom auf Gold, Ztschr. anorg. Chem., 3, 421.

1893. With K. Hofmann: Ueber die Terbinerde, Ztschr. anorg. Chem., 4, 27.

1893. With Anton Loose: Annähernde Bestimmung des Aequivalents seltener Erden durch Titration, Ztschr. anorg. Chem., 4, 161.

1893. With Conrad Volk: Zur Kenntniss der Schwefelverbindungen des Thoriums, Ztschr. anorg. Chem., 5, 75.

1894. Zur Kenntniss der Schwefelverbindungen des Thoriums, Ztschr. anorg. Chem., 6, 49.

1894. With Edmund Thiele: Ueber den Lösungszustand des Iod und die wahrscheinliche Ursache der Farbenunterschiede seiner Lösungen, Ztschr. anorg. Chem., 7, 52.

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## THE PROTEIDS OF THE RYE KERNEL.<sup>1</sup>

BY THOMAS B. OSBORNE.

Received April 2, 1895.

THE proteids of this seed have been but little studied and the statements published leave the subject in much confusion.

Einhof, who in 1805<sup>2</sup> undertook an analysis of rye, was the first to make observations on the proteids obtained therefrom. He found that an aqueous extract of rye-meal contained two distinct proteid substances, one coagulating on boiling, and insoluble in alcohol, which he called albumin, and the other not coagulating, but soluble in alcohol, which he called gluten [kleber]. The latter he considered to be identical with the similar substance extracted from wheat gluten by alcohol. Treatment with alcohol yielded much more "kleber" than was extracted by water alone. It is interesting to note that Einhof in this investigation first discovered that characteristic differences exist between different kinds of vegetable proteid matter, it being thought at that time that gluten and albumin were simply modifications of the same body which under like conditions would show the same properties.

Heldt<sup>3</sup> in 1843 published a description of the proteid taken up by alcohol from rye-meal. He prepared it by extracting the meal with hot alcohol, distilling off the alcohol, and treating the residue with ether to remove fat, and with water to remove ether and sugar.

This preparation was analyzed with the following result:

Carbon .....	56.38
Hydrogen .....	7.87
Nitrogen .....	15.83
Sulphur }	19.92
Oxygen }	

100.00

<sup>1</sup> From the report of the Connecticut Agricultural Experiment Station for 1894. Communicated by the author.

<sup>2</sup> *J. d. Chem. v. Gehlen*, 5, 131.

<sup>3</sup> *Ann. d. Chem. u. Pharm.*, 45, 195.

Heldt remarked, "the same composition was found by Scherer and Jones for other nitrogenous constituents of plants, plant-casein, plant-albumin, and plant-gelatin, to which last this body appears to stand nearest."

Jones<sup>1</sup> obtained albumin from rye by boiling the aqueous extract and treating the resulting coagulum with ether. He states that this albumin contained :

Carbon .....	54.74
Hydrogen.....	7.77
Nitrogen .....	15.85
Oxygen .....	21.64
	<hr/>
	100.00

Verdeil,<sup>2</sup> contrary to the experience of Einhof, von Bibra, Ritthausen, and the writer, obtained gluten from rye-meal by kneading and washing in a cloth until starch was removed. He states that there remained a tough, glutinous substance, which could be easily drawn into threads. This gluten he says was not pure but was contaminated with a substance soluble in alcohol. When thoroughly extracted with alcohol he considered it to be pure. He determined sulphur in the gluten and found 0.989 and 0.972 per cent. Von Bibra<sup>3</sup> considered the proteid extracted from rye by alcohol to be the same as that similarly obtained from wheat. He gave the nitrogen content of this body as 15.73, 15.52, and 15.50, and the sulphur as 0.973 and 0.950 per cent. He also recognized the presence of "casein" which he did not analyze, and found from 1.565 to 2.799 per cent. of albumin, which contained 15.53 and 15.42 per cent. of nitrogen. He considered the proteids of rye to be the same as those of wheat.

Rittenhausen<sup>4</sup> described three proteid substances which he found in rye; albumin, soluble in water, mucidin, soluble in alcohol, and gluten-casein, soluble in dilute potash water but insoluble in water and cold alcohol.

Albumin, he says, is present in the aqueous extracts but he made no further examination of this body. The mucidin he considers to be the only proteid, soluble in alcohol, present in

<sup>1</sup> *Ann. d. Chem. u. Pharm.*, 40, 66.

<sup>2</sup> *Ann. d. Chem. u. Pharm.*, 58, 319.

<sup>3</sup> *Die Getreidearten u. das Brod*, Nuernberg, 1860, 291.

<sup>4</sup> *J. prakt. Chem.*, 99, 439, and *Die Eiweisskoerper*, etc., Bonn. 1872, p. 83.

the rye kernel and this he regarded as similar to the mucedin which was believed to exist in the wheat kernel. He was unable to detect the presence of gliadin. Mucedin was prepared by extracting the meal with hot alcohol of eighty-five per cent. and concentrating and cooling the solution. The deposited substance was further extracted with alcohol and ether. It was then dissolved in acetic acid and fractionally precipitated with potash. He states the composition of the substance as :

Carbon .....	53.61
Hydrogen .....	6.79
Nitrogen .....	16.84
Sulphur.....	0.50
Oxygen .....	22.26
	<hr/>
	100.00

The gluten-casein was obtained by extracting the rye-meal directly with very dilute potash-water, precipitating with acetic acid and washing with water, alcohol, and ether. Two preparations were made and gave, as an average, the following figures on analysis :

Carbon....	52.14
Hydrogen .....	6.93
Nitrogen .....	16.38
Sulphur.....	1.06
Oxygen .....	23.49
	<hr/>
	100.00

Sidney Martin<sup>1</sup> states that wheat, rye, and barley contain a globulin substance similar in properties to animal myosin, being soluble in ten to fifteen per cent. sodium chloride solutions, precipitated therefrom by saturation with sodium chloride and with magnesium sulphate, and coagulating at 55° to 60°. This globulin is precipitated by dialysis and thereby is converted into the albuminate form. It is very evident from the foregoing summary of previous work that we have no satisfactory knowledge of the rye proteids.

In presenting the results of my investigation the subject may be most conveniently discussed under the following heads :

A, proteids soluble in water ; B, proteids insoluble in water

<sup>1</sup>*Jour. Physiol.*, 8, viii.

but soluble in saline solutions; C, proteids insoluble in water and in saline solutions but soluble in alcohol; and, D, proteids insoluble in water, saline solutions, or alcohol but soluble in dilute alkalis.

A. PROTEIDS SOLUBLE IN WATER. LEUCOSIN. PROTEOSE.

The proteids soluble in water are best examined in extracts made in the first instance with ten per cent. sodium chloride solution from which subsequently the soluble salts have been removed by prolonged dialysis. When water is applied to the grain it becomes a weak saline solution which not only takes up globulins but also extracts gliadin whose presence greatly complicates the examination of the water-soluble proteids. Rye-meal<sup>1</sup> was accordingly exhausted with a solution containing ten per cent. sodium chloride and the extract, after syphoning from the subsided insoluble matters, was freed from salts and globulin by dialysis in river water and filtration. The resulting solution yielded no more globulin by dialysis in distilled water and contained only those proteids extracted from the seed which were soluble in pure water. As the extract was bulky the proteids were precipitated by saturation with ammonium sulphate and thereupon dissolved in water. A comparatively concentrated solution was thus obtained which was very nearly freed from ammonium sulphate by dialysis. It then had the following properties: When heated slowly it became turbid at 52° and particulate at 63°. After filtering from this coagulum nothing more separated even on boiling. Saturation of the dialyzed solution with sodium chloride gave a precipitate that dissolved readily in water to a solution, which, heated to 63°, yielded a coagulum of albumin. The filtrate from this coagulum was again saturated with salt and a considerable precipitate obtained showing that with the albumin some proteose-like body was thrown down. Nitric acid added to the solution of this precipitate in water gave a precipitate which dissolved on warming and reappeared on cooling. The solution after filtering out the first precipitate of proteose and albumin, produced by saturation with sodium chloride, gave more precipitate on adding acetic

<sup>1</sup> The rye-meal used throughout this work was obtained by grinding, in the laboratory, portions of clean and fresh winter rye, as needed for each extraction.

acid, showing the presence of a further quantity of proteose. The coagulum above described, which separated on heating its solution to 65°, was washed thoroughly with water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. When dried at 110° it had the following composition :

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 1.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.31	....	52.31	52.57
Hydrogen .....	6.78	....	6.78	6.81
Nitrogen .....	16.14	16.11	16.13	16.22
Sulphur } .....	....	....	....	24.40
Oxygen }				
				100.00

Ash ..... 0.51

Another extract was examined in a slightly different way. 1,000 grams of rye-meal were extracted with eleven liters of ten per cent. sodium chloride solution and, in order to get rid of the large amount of gum taken up, the solution, after filtering, was dialyzed and then saturated with ammonium sulphate. The precipitate thus produced was dissolved, as far as possible, in ten per cent. sodium chloride brine, filtered clear, and dialyzed until chlorides were removed. The solution after filtering clear was then heated to 65° and the albumin that separated was filtered out, washed thoroughly with hot water, with alcohol, and with ether, and dried over sulphuric acid. This preparation, 2, weighed 1.21 grams and had the following composition :

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 2.*

		Ash-free.
Carbon .....	53.04	53.29
Hydrogen .....	6.70	6.74
Nitrogen .....	16.57	16.65
Sulphur } .....	....	23.32
Oxygen }		
		100.00

Ash..... 0.50

The solution containing the proteoses, filtered from preparation 2, was then treated with twenty per cent. of its weight of dry sodium chloride and a little two-tenths per cent. hydrochloric acid was added which gave a considerable precipitate.

This was filtered out, dissolved in distilled water, and the solution dialyzed till free from chlorides. This solution then gave a precipitate with nitric acid, which dissolved on warming and precipitated again on cooling. The solution concentrated to a syrup on a water-bath was precipitated by pouring into absolute alcohol. The precipitate, when dried over sulphuric acid, weighed 0.41 gram or one-third as much as the albumin. The filtrate, from the precipitation of this substance [with twenty per cent. of sodium chloride and acid], was saturated with ammonium sulphate and the precipitate thus produced filtered out and dissolved in distilled water. With copper sulphate and potash this substance gave a clear pink color. Its solution gave no precipitate on adding nitric acid until it had been saturated with sodium chloride, when a slight precipitate fell. It yielded no precipitate with copper sulphate. These reactions indicate that besides albumin the aqueous extract contains small quantities of proto- and deuterio-proteose.

Again, 2,000 grams of rye-meal were treated with ten per cent. sodium chloride solution and the extract filtered and saturated with ammonium sulphate. The precipitate produced was dissolved in ten per cent. sodium chloride solution, filtered, and dialyzed until all chlorides were removed. After filtering clear the solution was heated to 65° for some time and the coagulum filtered out, washed with hot water, alcohol, and ether, and dried for analysis, preparation 3. The filtrate from 3 was then concentrated by boiling, during which a coagulum developed. This was filtered out, washed as usual, and dried for analysis, preparation 4.

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 3.*

	I.	II.	Average.	Ash-free.
Carbon.....	53.41	53.32	53.37	53.52
Hydrogen .....	6.90	6.82	6.86	6.88
Nitrogen.....	16.73	....	16.73	16.78
Sulphur } .....	....	....	....	22.82
Oxygen } .....	....	....	....	22.82
				100.00
Ash.....	0.30			

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 4.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.64	52.53	52.58	52.86
Hydrogen .....	6.76	6.73	6.75	6.79
Nitrogen .....	16.86	....	16.86	16.95
Sulphur } .....	....	....	....	23.40
Oxygen }				
				100.00
Ash.....	0.56			

Another extract was made by treating 1,700 grams of rye-meal with sixteen liters of water. After standing over night the solution was filtered off and saturated with ammonium sulphate. The meal residue was treated again in the same way and the filtered extract, after saturating with ammonium sulphate, was added to that first obtained. The precipitated proteids were then dissolved in water yielding a very gummy solution. As this solution was bulky the proteids were again precipitated with ammonium sulphate and the precipitate after filtering out was treated with three liters of ten per cent. sodium chloride solution. The whole was then dialyzed, it having been found that these viscid solutions lost their gummy character on dialysis. After eight days all the gum had disappeared. The solution was then readily filtered clear. In order to reduce the volume of the solution it was again saturated with ammonium sulphate and the large precipitate treated with about a liter of ten per cent. sodium chloride solution. A turbid liquid resulted which was not cleared by passing through filter-paper but, on standing, became clear and the sediment was found to consist of gliadin, which is to be noticed later. Gliadin is soluble to a considerable extent in pure water and in water containing but a very small amount of dissolved salts, but the addition of a little sodium chloride to its solution precipitates it completely. After the solution had entirely cleared by subsidence it was dialyzed free from chlorides and heated to 65°. The resulting coagulum was then filtered out, washed and dried in the usual manner, and found to weigh 1.55 grams. The composition of this preparation was as follows:

[illegible]



Five hundred grams of rye flour<sup>1</sup> were extracted with 2,000 cc. of five per cent. sodium chloride solution and 1,000 cc. of the clear filtered extract were dialyzed till free from chlorides. The solution was then filtered and heated for twenty-four hours in a water-bath of 70°. The coagulated albumin was filtered out, washed with water, alcohol, and ether, and dried over sulphuric acid, and found to weigh 1.08 grams, equivalent to 0.43 per cent. of the flour.

So far as tested this albumin agrees in all respects with that obtained from wheat.<sup>2</sup> The variations in composition of these preparations are considerable but perhaps not greater than might be expected.

The aqueous and saline extracts of the rye-meal contain much gum and coloring matters which render the isolation of pure proteids very difficult. It will be seen, however, that the preparations of wheat albumin and rye albumin have very nearly the same average composition and that both proteids show the same reactions and coagulate at the same temperature. They are unquestionably the same substance, for which I have adopted the name *leucosin*.

## COAGULATED LEUCOSIN.

	Wheat. Average of five analyses.	Rye. Average of six analyses.
Carbon .....	53.02	52.97
Hydrogen .....	6.84	6.79
Nitrogen .....	16.80	16.66
Sulphur .....	1.28	1.35
Oxygen.....	22.06	22.23
	<hr/> 100.00	<hr/> 100.00

The proteoses of the rye also show the same reactions as those of the wheat kernel, and so far as it is possible to determine they are identical.

## B. PROTEID SOLUBLE IN SALINE SOLUTIONS. EDESTIN.

Owing to the large amount of gum extracted from the rye-meal, the preparation of the globulin in a pure state was found to be extremely difficult. Such preparations as were made disagreed

<sup>1</sup> Made by the Health Food Company of New York.

<sup>2</sup> *Am. Chem. J.*, 15, 408; also *Ann. Report Conn. Expt. Station for 1893*, p. 179.

in composition and in only one case was a substance obtained which appeared to be pure enough to warrant the publication of its analysis. So far as could be detected the globulin which separated on dialysis had the same properties as that similarly derived from wheat. One preparation of this globulin, which had nearly the same composition as the wheat globulin and appeared to be free from gum and other impurities, was obtained as follows: 5,000 grams of rye flour, made by the Health Food Co. of New York, were extracted with fifteen liters of five per cent. sodium chloride solution and the extract filtered clear. Nine liters of extract were thus obtained, being approximately equal to a complete extraction of three kilos of rye flour.

The entire solution was dialyzed for four days in order to remove the greater part of the gum. The extract was saturated with ammonium sulphate, the precipitate filtered out, suspended in water, and dialyzed for three days. Most of the substance was now dissolved and the insoluble matter was filtered out, washed with sodium chloride solution, and the filtrate and washings returned to the dialyzer. When free from chlorides the solution was filtered from a small precipitate and this latter washed with water, alcohol, and ether and dried over sulphuric acid. Only 1.21 grams of globulin were obtained, which, when dried at 110°, had the following composition:

RYE GLOBULIN, EDESTIN, *Preparation 7*. WHEAT GLOBULIN, EDESTIN.

		Ash-free.	Average of five analyses.
Carbon.....	51.03	51.19	51.03
Hydrogen .....	6.72	6.74	6.85
Nitrogen.....	18.14	18.19	18.39
Sulphur } .....		23.88	0.69
Oxygen } .....			23.04
Ash.....	0.33	<hr/>	<hr/>
		100.00	100.00

The writer has no doubt that this globulin is identical with the *edestin* found in the wheat kernel and other seeds,<sup>1</sup> but owing to the difficulties encountered in preparing it from rye, further evidence on this point was not obtained.

With reference to Martin's statement concerning the presence of myosin—what is written on that point in the paper by Osborne

<sup>1</sup> Annual Report Conn. Expt. Station for 1893, pp. 179 and 216.

and Voorhees on the "Proteids of the Wheat Kernel" applies equally to rye.<sup>1</sup>

### C. PROTEID SOLUBLE IN ALCOHOL. GLIADIN.

After extraction with sodium chloride solution, alcohol of seventy-five to eighty per cent. takes up a considerable quantity of proteid. One hundred grams of rye-meal were extracted thoroughly with ten per cent. sodium chloride solution and then with seventy-five per cent. alcohol. The alcoholic extract was evaporated to very small volume and the separated proteid washed with water and ether and then dried. It weighed 3.93 grams, being therefore nearly four per cent. of the meal. Two thousand grams of rye-meal were then extracted with alcohol of 0.9 specific gravity, four successive times. Each extract, after filtering clear, was concentrated by distillation on a water-bath. The first three extracts yielded, on cooling, a deposit of proteid, but the fourth contained almost none. Each residue was then washed with water and dissolved in seventy-five per cent. alcohol. The substance from the first extract yielded an insoluble residue which, when washed with dilute alcohol, absolute alcohol, and ether, gave preparation 8. This dried at 110° contained seventeen per cent. of nitrogen. The solutions of the substances from the three extracts in dilute alcohol, were concentrated to about one-fourth their original volume and cooled, when the dissolved proteid separated. The substance from the first extract was digested with absolute alcohol which dissolved a part of it, then with ether, and dried, giving preparation 9. The residue from the second extract was washed superficially with water and then treated in a divided state with distilled water until dissolved. A little saturated sodium chloride was then added and the proteid wholly precipitated. The precipitate was then thoroughly dehydrated with absolute alcohol, digested with ether, and dried. This formed preparation 10. The proteid separated from the third extract was digested with absolute alcohol and with ether, and yielded a small quantity of proteid, preparation 11, which when dried contained, ash-free, 16.89 per cent. of nitrogen. The absolute alcohol used in dehydrating preparation 9, with help of the water which it extracted, dissolved a con-

<sup>1</sup>*Am. Chem. J.*, 15, 415.

siderable quantity of proteid. This was precipitated by adding a few drops of sodium chloride solution. The precipitate produced was then digested with absolute alcohol and ether and, when dried was found to contain, ash-free, 16.02 per cent. of nitrogen. The preparation was therefore redissolved in dilute alcohol, filtered perfectly clear, concentrated to small volume, and cooled. The proteid separating was then treated as before with absolute alcohol and ether and yielded preparation 12. The proteid thus extracted showed in all respects the properties of wheat gliadin, and it will be seen that it has nearly the same composition.

RYE GLIADIN, *Preparation 9.*

	I.	II.	Average.	Ash-free.
Carbon .....	52.76	....	52.76	52.84
Hydrogen .....	6.81	....	6.81	6.82
Nitrogen .....	17.14	17.23	17.19	17.22
Sulphur } .....	....	....	....	23.12
Oxygen } .....	....	....	....	23.12
Ash .....	0.16			100.00

RYE GLIADIN, *Preparation 10.*

	I.	II.	Average.	Ash-free.
Carbon .....	53.06	52.90	52.98	53.23
Hydrogen .....	6.83	7.11	6.97	7.00
Nitrogen .....	17.13	17.17	17.15	17.23
Sulphur } .....	....	....	....	22.54
Oxygen } .....	....	....	....	22.54
Ash .....	0.48			100.00

RYE GLIADIN, *Preparation 12.*

	I.	II.	Average.	Ash-free.
Carbon .....	52.99	53.11	53.05	53.11
Hydrogen .....	6.73	6.83	6.78	6.79
Nitrogen .....	17.57	....	17.57	17.59
Sulphur .....	1.44	....	1.44	1.44
Oxygen .....	....	....	....	21.07
Ash .....	0.12			100.00

One thousand grams of rye-meal were thoroughly extracted with ten per cent. sodium chloride solution and drained as dry as possible on filters. The extracted residue was then treated with alcohol of 0.860 specific gravity four consecutive times. The four red-brown extracts were filtered clear, concentrated till most

of the alcohol was removed, and then cooled. The precipitates thus obtained were united and treated at first with stronger and afterwards with seventy-five per cent. alcohol until all soluble was dissolved. A considerable residue remained which appeared to be coagulated gliadin. This was washed thoroughly with absolute alcohol and ether, and when dried weighed 5.62 grams, preparation 13. The dissolved proteid, after filtering its solution perfectly clear, was separated by concentrating to small volume and cooling. The deposit was then treated with absolute alcohol, dissolved again in a little dilute alcohol, and precipitated by pouring into absolute alcohol. The proteid, preparation 14, separated perfectly colorless, in a finely divided state. When dried it weighed 11.66 grams.

RYE GLIADIN, *Preparation 13.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.36	....	52.36	52.62
Hydrogen .....	6.73	....	6.73	6.76
Nitrogen .....	17.75	17.59	17.67	17.75
Sulphur.....	1.19	....	1.19	1.19
Oxygen .....	....	....	....	21.68
				<hr/> 100.00
Ash .....	0.51			

RYE GLIADIN, *Preparation 14.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.74	....	52.74	52.93
Hydrogen .....	6.73	....	6.73	6.75
Nitrogen .....	17.32	17.52	17.42	17.48
Sulphur.....	1.23	....	1.23	1.23
Oxygen .....	....	....	....	21.61
				<hr/> 100.00
Ash .....	0.37			

These two preparations formed together 1.73 per cent. of the rye-meal and have the composition of wheat gliadin. In order to prevent contamination of this proteid with the gum contained in rye-meal, which Ritthausen<sup>1</sup> states to be freely soluble in fifty per cent. alcohol, the following method was tried:

After extracting rye-meal with ten per cent. sodium chloride

<sup>1</sup> Die Eiweisskörper, etc., Bonn, 1872, p. 96, and *J. prakt. Chem.*, 99, 454, and 102, 321.

brine, the residue was treated with alcohol so strong that with the water retained by the meal, a mixture resulted containing about seventy-five per cent. of alcohol. After standing over night the extract was syphoned from the residue and greatly diluted with water. The proteid separated on standing and was filtered out and dissolved in seventy-five per cent. alcohol. This solution was filtered perfectly clear, concentrated, cooled, and the separated proteid treated with absolute alcohol and ether and dried. The resulting preparation 15, was perfectly white. The residual meal was again extracted with seventy-five per cent. alcohol and the extract filtered clear, concentrated to one-fourth its volume, cooled, the precipitated proteid again dissolved in seventy-five per cent. alcohol, filtered clear, concentrated, cooled, and the separated proteid washed repeatedly with water. The substance was again dissolved in dilute alcohol and the clear solution precipitated by pouring into absolute alcohol. The precipitate produced was still again dissolved in dilute alcohol and a second time precipitated by pouring into absolute alcohol. The precipitate thus resulting was dissolved in dilute alcohol and precipitated by pouring into water and adding a little salt. The final pure white precipitate was digested with absolute alcohol and ether and dried, giving preparation 16.

RYE GLIADIN, *Preparation 15.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.03	52.09	52.06	52.40
Hydrogen.....	6.78	6.91	6.85	6.89
Nitrogen.....	17.80	....	17.80	17.91
Sulphur.....	1.23	....	1.23	1.24
Oxygen.....	....	....	....	21.56
				<hr/>
Ash.....	0.68			100.00

RYE GLIADIN, *Preparation 16.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.74	52.65	52.70	53.03
Hydrogen.....	6.90	6.96	6.93	6.97
Nitrogen.....	17.39	....	17.39	17.50
Sulphur.....	1.29	....	1.29	1.30
Oxygen.....	..	....	....	21.20
				<hr/>
Ash.....	0.65			100.00

Another preparation of this substance was made by extracting three thousand grams of rye flour directly with seventy-five per cent. alcohol. The extract was concentrated to one-fourth its volume and the proteid which separated on cooling was washed many times with distilled water and dissolved in dilute alcohol, yielding a clear solution. This was then poured into three times its volume of absolute alcohol and an opalescent mixture obtained which deposited a curdy precipitate after adding a little sodium chloride solution. The strong alcoholic solution from which this separated was clear and of a deep yellow color. The precipitate was treated with absolute alcohol as long as this was colored. During the process the substance was rubbed up to a fine powder. It was finally digested with ether for twenty-four hours and dried over sulphuric acid. This preparation, 17, weighed fifty-eight grams, and was perfectly white. It formed very nearly two per cent. of the meal.

RYE GLIADIN, *Preparation 17.*

Carbon.....	52.68
Hydrogen .....	6.71
Nitrogen .....	17.89
Sulphur.....	1.22
Oxygen .....	21.50
Ash.....	0.00

---

100.00

In order to establish conclusively whether more than one alcohol-soluble proteid is contained in the rye kernel, five preparations were made from the same portion of meal, by fractional precipitation. Four thousand grams of rye-meal were thoroughly extracted with ten per cent. sodium chloride solution, and the greater part of the bran removed by washing the meal through coarse cloth with the salt solution. The residue, after decanting the salt solution, was extracted with seventy-five per cent. alcohol; the extract was filtered clear and divided into two parts. The first part was concentrated to one-fourth and cooled, the second to one-half. The precipitated proteid from each was washed repeatedly with distilled water, dissolved in a small amount of seventy-five per cent. alcohol, filtered clear, and pre-

cipitated by pouring into absolute alcohol. The proteid thus separated was digested with absolute alcohol and with ether. From the first portion of the alcoholic extract, preparation 18 was obtained, from the second, preparation 19. These had the following composition :

*RYE GLIADIN, Preparation 18.*

		Ash-free.
Carbon.....	51.90	52.67
Hydrogen .....	6.87	6.97
Nitrogen .....	17.50	17.76
Sulphur .....	1.26	1.27
Oxygen .....	....	21.33
		<hr/>
		100.00
Ash .....	1.48	

*RYE GLIADIN, Preparation 19.*

		Ash-free.
Carbon .....	52.04	52.40
Hydrogen .....	6.66	6.71
Nitrogen .....	17.77	17.89
Sulphur .....	1.15	1.16
Oxygen.....	....	21.84
		<hr/>
		100.00
Ash .....	0.71	

The water washings from these two preparations were severally mixed with a little saturated sodium chloride solution which gave a considerable precipitate in each. These precipitates were then washed superficially with distilled water, dehydrated with absolute alcohol, and treated with ether. The washings from 18 yielded preparation 20, those from 19, preparation 21.

*RYE GLIADIN, Preparation 20.*

	I.	II.	Average.	Ash-free.
Carbon .....	51.36	51.55	51.46	53.05
Hydrogen .....	7.07 <sup>1</sup>	6.61	6.61	6.92
Nitrogen.....	17.64	17.61	17.63	18.17
Sulphur .....	1.14	....	1.14	1.17
Oxygen .....	....	....	....	20.69
				<hr/>
				100.00
Ash .....	3.01			

<sup>1</sup> Omitted in average.





Comparing these results with those obtained by Osborne and Voorhees in analyzing gliadin from wheat<sup>1</sup> it is seen that they agree very closely, similar variations between the analyses existing in both cases. The averages of the two series of analyses agree well, as shown by the following figures :

GLIADIN.		
	Wheat.	Rye.
Carbon .....	52.72	52.75
Hydrogen .....	6.86	6.84
Nitrogen .....	17.66	17.72
Sulphur .....	1.14	1.21
Oxygen .....	21.62	21.48
	<hr/> 100.00	<hr/> 100.00

In all their properties wheat gliadin and rye gliadin resemble each other so exactly as to leave no doubt of their chemical identity. Ritthausen, as already stated, failed to find gliadin in rye-meal and described the proteid soluble in alcohol as mucedin, having a lower nitrogen and higher carbon content. This disagreement is doubtless due to impurities in Ritthausen's preparations, which, as he mentions, contained coloring matter that could not be removed. This color was probably a result of extracting with hot alcohol, which Ritthausen appears to have used in all cases, cold alcohol having given him a small yield of proteid. I had, however, no trouble in obtaining an abundant yield of gliadin with cold alcohol of seventy per cent., and thereby have extracted far less coloring matter than with hot alcohol.

#### D. PROTEID SOLUBLE ONLY IN DILUTE ALKALIES.

The sample of rye flour previously used in this work contained 1.52 per cent. of nitrogen. The amount of nitrogen soluble in salt solution and in dilute alcohol was determined in this flour by extracting 100 grams with a large quantity of five per cent. sodium chloride solution and then with seventy-five per cent. alcohol. The residue was then thoroughly air-dried and found to weigh seventy-eight grams. This residue contained 0.55 per cent. of nitrogen. The 100 grams of flour therefore con-

<sup>1</sup> *Am. Chem. J.*, 15, 436.

tained 1.52 grams of nitrogen of which 0.43 gram remained after extraction and 1.09 grams were soluble in dilute salt solution and alcohol, or in other words, 71.7 per cent. of the nitrogen was soluble in the reagents named and 28.3 per cent. was insoluble. In the wheat kernel a considerable part of the nitrogen was likewise found to be insoluble in salt solution and in dilute alcohol, but as this substance could be separated as a constituent of the gluten it was possible to prepare it in quantity and in a state of comparative purity. Since rye flour yielded no gluten on washing with water, the proteid remaining in the meal after extracting with salt solution and dilute alcohol, could be obtained only by extracting the residual meal directly with dilute potash water. All attempts, however, to thus prepare this substance resulted only in the production of small preparations of very variable composition. The gum present in the seed dissolved freely in the alkaline solution and made it impossible by any means yet discovered to thoroughly purify the preparations. For this reason nothing positive can be said now in relation to the nature or composition of this residual proteid. Since the other proteids are the same as those found in the wheat kernel it might be conjectured that this proteid is identical with glutenin. The fact that rye flour yields no gluten is, however, opposed to such a conclusion. It is therefore more probable that the substance in question is, partly or wholly, other than glutenin.

#### QUANTITIES OF THE DIFFERENT PROTEIDS IN THE RYE KERNEL.

Owing to the gum already mentioned the filtration and treatment of the rye extracts was difficult and prolonged and the amounts of globulin, albumin, and proteose could not be determined separately, as in the case of wheat. The rye flour contained 1.52 per cent. of nitrogen. If we assume that the proteids of rye contain on the average 17.6 per cent. of nitrogen, as was very nearly the case with those of wheat, and that all the nitrogen exists in proteid form, this sample of flour would contain 8.63 per cent. of proteid. We have, therefore, 2.44 per cent. of insoluble proteid and 6.19 per cent. soluble in salt solution and alcohol. We have already shown that the alcohol-soluble gliadin amounted to four per cent. of the flour and the

leucosin to 0.43 per cent.; there thus remains 1.76 per cent. to be divided between edestin and proteoses.

Insoluble in salt solution.....	2.44 per cent.
Gliadin, soluble in alcohol .....	4.00 "
Leucosin, soluble in water .....	0.43 "
Edestin and Proteose, soluble in salt solution	1.76 "
	<hr/> 8.63 "

### ZIRCONIUM SULPHITE.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 30, 1895.

VERY little is recorded in the text-books on chemistry with regard to this compound of zirconium. Berthier is reported as having examined it and found it to be a white insoluble body, slightly soluble, however, in an aqueous solution of sulphurous acid; from which it is thrown down again upon boiling. Whether this was what is commonly known as the neutral, or the acid, or a basic sulphite, is not recorded. It is highly probable that with so weak an acid as sulphurous acid, zirconium would form under these circumstances only basic compounds. We may state with regard to our own work that we have been unable with one exception to form any sulphite corresponding to the acid or the neutral. Only very indefinite compounds or mixtures of the sulphite with the hydroxide have come into our hands, as a rule.

The subject was first brought to our attention by the study of the reaction utilized by Baskerville for the quantitative separation of zirconium from iron and aluminum.<sup>1</sup> It was also put into use by him for shortening the method of preparing the pure zirconium chlorides.<sup>2</sup> The reaction in question is that which takes place when a nearly neutral solution of zirconium chloride is boiled with sulphur dioxide in excess.

Several points of interest were observed as to this reaction. It was found that when a solution of the sulphate was used it was difficult to secure any precipitation by means of sulphur dioxide even with persistent boiling. The chloride was clearly

<sup>1</sup> THIS JOURNAL, 16, 475.

<sup>2</sup> J. Elisha Mitchell, Scientific Society, 11, 85.

the best salt to use. The pure chloride was made up into approximately a two and a half per cent. solution and this was either very nearly neutralized by means of ammonia, or ammonia was added until there was a slight permanent precipitate. In the latter case the saturation of this solution with sulphur dioxide produced an immediate precipitate. If this were permitted to stand for some time the precipitate was redissolved, the remaining liquid being only slightly clouded. This re-solution was probably due to the hydrochloric acid liberated and also to the excess of sulphurous acid present. If this solution of zirconium chloride saturated with sulphur dioxide were diluted with several times its volume of water and boiled from fifteen to thirty minutes, a heavy white precipitate was produced. This was quite easily filtered by means of an unglazed porcelain suction filter. The precipitate was washed several times and finally dried over sulphuric acid in a desiccator. The analysis gave :

Zirconium dioxide.....	61.10	61.75	61.75	61.00	....	....
Sulphur dioxide.....	....	....	....	....	22.24	22.20
Ratio of zirconium to sulphur dioxide is 2 : 1, approximately.						
Ratio of zirconium to sulphur dioxide in the neutral sulphite, $Zr(SO_3)_2$ , is 1 : 1.4.						

This substance when so dried was perfectly white and quite hard. It was powdered with some difficulty in an agate mortar and resembled very much finely divided silica.

It was sometimes noted that the precipitate formed on passing the sulphur dioxide into the solution of zirconium chloride was partially dissolved upon the prolonged passage of the gas. To determine in how far the liberated hydrochloric acid was the agent causing this re-solution, some zirconium hydroxide, freshly precipitated by means of ammonium hydroxide, was washed free from hydrochloric acid and was then treated with a concentrated and freshly prepared solution of sulphur dioxide. This was allowed to stand during two or three months and was frequently shaken. The solid at the bottom of the flask separated into two layers, the gelatinous hydroxide settling first and upon this a white finely divided substance formed. The supernatant liquid was found to contain zirconium. The white layer was separated from the hydroxide and analyzed. It contained :

Zirconium dioxide .....	15.05	15.53	....
Sulphur dioxide.....	....	....	4.86
Water (blast-lamp).....	2.78	3.03	....
Water, at 95° C.....	77.41	76.33	....
	<hr/>	<hr/>	
	100.10	99.75	

Ratio of zirconium to sulphur dioxide is 2.2 : 1.

This substance apparently came to a constant weight on drying in a steam-bath at 95° C.

A somewhat peculiar product was obtained during an attempt at filtering the precipitated sulphite. It filtered very slowly and in the course of a few hours a layer of a watery liquid formed above the white sulphite. This was allowed to stand several days and turned into a solid jelly. This was noticed several times. The thickness of the jelly-like layer would, of course, depend upon the amount of moisture in the precipitate but several times it was half an inch or more in thickness. This body was analyzed in the moist condition after simply drying between filter-paper. It gave :

Zirconium dioxide.....	20.02	20.65	....	....
Sulphur dioxide.....	....	....	5.19	5.51
Water (blast-lamp).....	9.14	8.53	....	....
Water, at 95° C.....	65.65	65.22	....	....
	<hr/>	<hr/>		
	100.00	99.91		

Ratio of zirconium and sulphur dioxide is here 3 : 1.

A portion of this jelly was brought to constant weight by heating for a number of hours in a steam-bath. About sixty-five per cent. of the original weight was lost and the body assumed a translucent appearance like dried gelatine. The analysis of this gave :

Zirconium dioxide.....	59.34	....
Sulphur dioxide .....	....	11.46
Water (blast-lamp) .....	29.20	...
	<hr/>	
	100.00	

Ratio of zirconium to sulphur dioxide is 4 : 1.

The analysis shows that some of the sulphur dioxide was lost on drying.

It will be seen then that these different preparations show a

very varying ratio of the zirconium to the sulphur dioxide and in no case approach to the ratio of the neutral sulphite (1 : 1.4). They are, therefore, to be looked upon as either mixtures of the sulphite and hydroxide or very unstable compounds. The jelly-like substance mentioned last gives more promise of being a chemical individual; still it has not been thought legitimate to attempt the calculation or assignment of a formula to it.

A last attempt at preparing the neutral sulphite was made by placing some of the excess of sulphurous acid, which had been standing over the precipitated zirconium sulphite, in a dessicator and allowing it to evaporate over sulphuric acid. The bulk of liquid decreased from about 200 cc. to five to ten cc. and then hard, white, warty crystals began to form, which were quite difficult to remove from the crystallizing dish. In appearance they resembled zirconium sulphate. The solution had lost the odor of sulphur dioxide. The time consumed in the evaporation was several months.

The crystals were dried upon filter-paper and yielded, on analysis,

Zirconium.....24.47 per cent.: on a dry basis, 36.43.

Sulphur dioxide 34.54      "      "      "      "      51.42.

Calculated for  $\text{Zr}(\text{SO}_3)_2$ , Zr 36.25;  $\text{SO}_3$  51.20. These crystals then seem to be a hydrated sulphite of the composition  $\text{Zr}(\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ .

The nature of the precipitate gotten by means of sodium sulphite was also examined. The sulphite used was fairly pure. The zirconium chloride solution was distinctly acid and the mixed solution was acid. A transient precipitate was produced in the cold on mixing the two. On heating, a good flocculent precipitate was formed which settled well and was easily filtered. The precipitate looked like the hydroxide, rather than the white sulphite already described. The analysis gave:

Zirconium dioxide..... 5.75    5.75    ....    ....

Sulphur dioxide..... ....    ....    1.05    1.004

Ratio of zirconium and sulphur dioxide is 4 : 1.

Chancel<sup>1</sup>, in giving a method of separation of iron from zirconium, states that by means of a boiling solution of sodium thio-

<sup>1</sup> *Ann. d. Chem. u. Pharm.*, 108, 237; *Watt's Dictionary*, 5, 1081, 1877.

sulphate the zirconium is precipitated as thiosulphate. Stromeier<sup>1</sup> stated that if a dilute zirconium chloride solution be neutralized by sodium carbonate in the cold and sodium thiosulphate added until the solution was decolorized and then boiled as long as sulphur dioxide came off, the zirconium would be precipitated as oxide (meaning doubtless hydroxide).

To test these observations a solution of zirconium chloride was neutralized by ammonia and an excess of sodium thiosulphate was added in crystals. A precipitate began to be formed directly. This was washed eight or ten times by decantation, filtered, the precipitate dried by absorption paper, and analyzed. It gave:

Zirconium dioxide.....	19.66	20.50	....	....
Sulphur dioxide .....	....	....	4.03	4.14
Water (blast-lamp) .....	16.05	16.41	....	....
Water, at 95° C.....	60.11	58.58	....	....
	<hr/>	<hr/>		
	99.85	99.61		

Percentage of zirconium on a water-free basis is 75.

Percentage of zirconium calculated in  $Zr(S_2O_3)_2$  is 21.95.

A second experiment was carried out with an acid solution of zirconium chloride. The sodium thiosulphate crystals were added in the cold and when completely dissolved the solution was heated to boiling. This precipitate on analysis gave :

Zirconium dioxide.....	21.74	20.73	....	....
Sulphur dioxide.....	....	....	5.33	5.41
Water (blast-lamp).....	9.72	8.64	....	....
Water, at 95° C.....	63.28	65.37	....	....
	<hr/>	<hr/>		
	100.07	100.15		

Finally another portion was taken, precipitated with an excess of sodium thiosulphate, and boiled until there was no longer any odor of sulphur dioxide. This precipitate was analyzed :

Zirconium dioxide.....	47.01	47.19	....	....
Sulphur dioxide.....	....	....	6.90	6.95
Water (blast-lamp).....	21.41	21.14	....	....
Water, at 95° C.....	24.16	24.72	....	....
	<hr/>	<hr/>		
	99.48	100.01		

The low percentage of water here was due to the exposure of

<sup>1</sup> *Ibid*, 113, 127.



the precipitate in a warm room and its consequent partial drying. There is no evidence here nor in the previous cases of the formation of any definite thiosulphate and we would question its existence under ordinary conditions. There is no evidence of the formation here of an hydroxide as one of the authors quoted states. Basic salts seem to be the only products.

UNIVERSITY OF NORTH CAROLINA,  
March, 1895.

### ON SOME CONDITIONS AFFECTING THE ACCURACY OF THE DETERMINATION OF POTASH AS POTAS- SIUM PLATINICHLORIDE.

BY A. L. WINTON, Connecticut Agricultural Experiment Station.

Received April 2, 1895.

IN the course of some determinations of potash in potassium chloride, made by direct evaporation with platinum solution preliminary to a further study of methods, it was observed that the potassium platinichloride was more finely divided and the results were higher when the solution of the potash salt was concentrated on adding the reagent, than when it was dilute.

In order to ascertain the real connections of the facts observed, I then made a series of experiments which were all conducted in exactly the same way, except for the kind of dish used, the dilution of the solution of potassium chloride on adding the platinum solution, the presence or not of added hydrochloric acid, the temperature of the water-bath, and the strength of alcohol used for washing.

The potassium chloride used was from a lot sent by Dr. H. J. Wheeler, Reporter on Potash, for the Association of Official Agricultural Chemists. After being finely ground, it contained 0.45 per cent. of moisture, which was determined by heating below a red heat over a lamp until constant weight was secured. In each case, approximately one-half gram was weighed out from a weighing bottle. After solution in water and adding platinum solution, the mixture was evaporated to a pasty condition, and about twenty-five cc. of alcohol were added and allowed to stand on the potassium platinichloride for one hour with repeated stirring. The precipitates were then collected in

Gooch crucibles, washed with about 100 cc. of alcohol, and dried to constant weight, first at 100° C. and finally at 130° C. The results calculated to potassium chloride by the use of the factor 0.3056 and expressed in per cents. of the quantity taken, are given in Table I.

It will be seen from the table that neither the kind of dish used, nor the temperature of the solution of potassium chloride on adding the platinum solution, nor the presence of a large excess of hydrochloric acid, during evaporation, nor the temperature of evaporation, had any perceptible influence on the results.

These points, therefore, need not be further considered. In most of the experiments ninety-five per cent. alcohol was used in order to diminish the solubility of the potassium platinichloride. In experiments Nos. 9, 10, 29, and 30, however, the alcohol was eighty per cent., and the results are, for this reason, somewhat lower.

*The Effect of Dilution of the Solution when Potassium Chloride with no Admixture is used.*—The principal point brought out by the experiments is the effect of the dilution of the potassium chloride solution when chloroplatinic acid is added, on the character of the potassium platinichloride, and the results.

If the potassium chloride were dissolved in fifty cc. of water, the potassium platinichloride was either not precipitated at all on addition of the platinum solution, or else went into solution when the liquid became heated, and was then deposited slowly on evaporation.

The potassium platinichloride thus obtained was invariably in brilliant, orange-colored granular crystals, which were often united to form plates from one to five mm. across. Constant weight was secured after drying the double salt for three hours at 100° C., the results of several determinations being concordant and slightly below theory. The loss on further drying at 130° was very small.

But if, on the other hand, ten cc. or less of water were used to dissolve the potassium chloride, a considerable portion of the potassium platinichloride precipitated as a fine powder immediately on adding the reagent, the remainder being deposited on evaporation. After treating with alcohol and filtering,

TABLE I.  
DETERMINATIONS OF POTASSIUM CHLORIDE UNDER VARIOUS CONDITIONS.  
(*Weight*  $K_2PtCl_6 \times 0.3056 = \text{weight } KCl$ .)

No. of experiment.	cc. water used to dissolve KCl.	cc. HCl concentrated added.	$H_2PtCl_6$ added to hot or cold solution.	Water-bath boiling or below boiling.	Volume per cent. of alcohol used for washing.	Kind of dish used for evaporation.	Grams of dry KCl taken.	Per cent. of KCl found.	
								$K_2PtCl_6$ dried at 100° C.	$K_2PtCl_6$ dried at 130° C.
1	50	0	Cold.	Boiling.	95	Porcelain.	0.4632	99.87	99.87
2	50	0	Hot.	"	95	Platinum.	0.4852	99.84	99.80
3	50	0	"	"	95	Porcelain.	0.4398	99.84	99.78
4	50	0	"	"	95	Platinum.	0.4696	99.82	99.76
5	50	0	"	Below boiling.	95	Porcelain.	0.4688	99.85	99.85
6	50	0	"	Boiling.	95	Platinum.	0.5194	99.82	99.82
7	50	0	"	"	95	Porcelain.	0.4602	99.87	99.85
8	50	0	"	"	80	Platinum.	0.4666	99.84	99.84
9	50	0	"	"	80	Porcelain.	0.4500	99.77	99.69
10	50	0	"	"	80	Platinum.	0.5005	99.76	99.70
11	25	0	"	"	95	Porcelain.	0.4090	100.17	100.01
12	25	0	Cold.	"	95	Platinum.	0.4485	99.97	99.97
13	25	0	Hot.	"	95	Porcelain.	0.4676	99.84	99.77
14	25	0	"	"	95	Platinum.	0.5107	99.69	99.64
15	25	0	Cold.	"	95	Porcelain.	0.5162	100.12	99.93
16	25	0	Hot.	"	95	Platinum.	0.4823	99.80	99.71
17	25	0	Hot.	"	95	Porcelain.	0.5095	100.06	100.00
18	25	0	Cold.	"	95	Platinum.	0.4643	99.69	99.64
19	10	0	"	"	95	Porcelain.	0.5371	100.33	100.08
20	10	0	Hot.	"	95	Platinum.	0.5183	100.47	100.16
21	10	0	Hot.	"	95	Porcelain.	0.4445	100.31	100.40
22	10	0	Cold.	"	95	Platinum.	0.4877	100.18	100.08
23	8	0	"	"	95	Porcelain.	0.5185	100.36	100.14
24	8	0	Hot.	"	95	Platinum.	0.4769	100.31	100.08
25	8	0	"	"	95	Porcelain.	0.5083	100.19	100.19
26	8	0	"	"	95	Platinum.	0.4782	100.30	100.27
27	8	0	"	Below boiling.	95	Porcelain.	0.5063	100.39	100.27
28	8	0	"	Boiling.	95	Platinum.	0.4632	100.47	100.25
29	8	0	"	"	80	Porcelain.	0.5088	100.42	100.25
30	8	0	"	"	80	Platinum.	0.5088	100.99	99.95

the salt presented the appearance of a fine, yellow powder, with generally an occasional granular crystal. Constant weight at  $100^{\circ}$  was only secured after heating from nine to fifteen hours, the results, although not always concordant, being in every case considerably above theory. Heating for many hours at  $130^{\circ}$  C. further reduced the results, although even after this treatment they were still slightly above theory.

The difference in the results obtained in dilute and concentrated solutions, is brought out strikingly by the averages given in the following table :

TABLE II.  
AVERAGES OF RESULTS OBTAINED IN DILUTE AND CONCENTRATED SOLUTIONS OF POTASSIUM CHLORIDE.

Dilution of the solution on adding $H_2PtCl_6$ .	Vol. per cent. of alcohol.	Average of results of expts. — Nos. —	Per cent. KCl found.	
			$K_2PtCl_6$ dried at $100^{\circ}$ C.	$K_2PtCl_6$ dried at $130^{\circ}$ C.
50 cc.	95	1 to 9	99.84	99.82
10 cc. or less	95	19 " 29	100.38	100.17
50 cc.	80	9 and 10	99.77	99.69
5 "	80	29 " 30	100.20	99.98

The average of eight closely agreeing results, using fifty cc. of water and ninety-five per cent. alcohol and drying at  $100^{\circ}$  C. is 99.84 per cent. potassium chloride. After drying at  $130^{\circ}$  C. the average is only 0.02 per cent. lower. But where the conditions were the same, except that only ten cc. or less of water were used to dissolve the potassium chloride, the average of ten results is 100.38 per cent. potassium chloride, after drying at  $100^{\circ}$  C., and 100.17 per cent. or 0.21 per cent. lower, after drying at  $130^{\circ}$  C. The results after drying at  $100^{\circ}$  C. and  $130^{\circ}$  C. are, on an average, 0.16 and 0.18 per cent. respectively below theory, whereas in concentrated solutions they are 0.38 and 0.17 per cent. respectively, above theory.

The results, using eighty per cent. alcohol, although all rather lower, show similar differences.

In the cases where the potassium chloride was dissolved in twenty-five cc. of water the results generally agree with those where fifty cc. of liquid was present, although not always.

In Table III are given the per cents. of potassium chloride corresponding to the average losses in weight of the potassium

platinichloride during successive periods at 100° and 130° C., in the case of ten determinations using fifty cc. of water and of twelve using ten cc. or less of water.

TABLE III.

SHOWING THE AVERAGE RATE OF DRYING OF POTASSIUM PLATINICHLORIDE OBTAINED FROM DILUTE AND CONCENTRATED SOLUTIONS.

(The first heating of three hours at 100° C. is not considered.)

K <sub>2</sub> PtCl <sub>6</sub> heated at	Percent of KCl corresponding to loss in weight of K <sub>2</sub> PtCl <sub>6</sub> .	
	Dilute solutions. Average of expts. Nos. 1 to 11.	Concentrated solutions. Average of expts. Nos. 19 to 31.
100° C. 3 hours.....	0.019	0.062
3 " .....	0.003	0.036
3 " .....	0.003	0.022
3 " .....	0.000	0.003
Total....	0.025	0.123
130° C. 7 hours.....	0.025	0.088
7 " .....	0.006	0.058
7 " .....	0.000	0.035
7 " .....	0.000	0.020
7 " .....	0.000	0.010
7 " .....	0.000	0.003
Total.....	0.031	0.214
100° and 130° total.....	0.056	0.337

*The Effect of the Dilution of the Solution when Potassium Chloride with other Salts and Sulphuric Acid is used.*—Following a method, such as the so-called alternate method of the Association of Official Agricultural Chemists, the solution to which platinum solution is added, should contain only sodium and potassium chlorides, having been previously freed from other matters.

In experiments Nos. 33 and 34, in Table IV, the solution contains about one part of potassium chloride to one and one-half parts sodium chloride, which is the ratio of these salts in kainite, the richest in soda of the commercial potash manure salts. In experiments Nos. 35 and 36, the ratio of the two salts, is approximately as one to one-half.

In analyses by the Lindo-Gladding method, however, part or all of the potash may exist as sulphate in the solution to which platinum solution is added and sodium and magnesium sulphates and chlorides may also be present.

In experiments Nos. 37 and 38 about the same proportions of magnesium sulphate as would be present in kainite were added, and in experiments Nos. 39 and 40 two parts of sulphuric acid were added to one part of potassium chloride.

In all these experiments platinum dishes were used, no hydrochloric acid was added, the platinum solution was added to the hot solution of the salts, the evaporation was carried on over boiling water-baths, and eighty per cent. alcohol was used for washing. The quantities of potassium chloride taken varied from 0.24 to 0.50 gram. In the case of experiments Nos. 37 and 38, where magnesium sulphate was present, the potassium platinichloride, after being collected on Gooch crucibles, was washed with 150 cc. of Gladding's reagent,<sup>1</sup> and then with eighty per cent. alcohol.

The double salt was, in each case, not only dried at 100° and 130°, but also at 160° C. In other respects the work was conducted as described for previous experiments. Results are given in Table IV.

In these experiments the dilution of the solution had the same effect on the form of the potassium platinichloride, the rate of drying, and the results obtained as in those previously made on potassium chloride alone.

The granular crystals obtained from dilute solutions after drying for two hours at 100° did not lose more than 0.06 per cent. during subsequent heating of many hours at 100°, 130°, and 160° C., the pulverulent form precipitated in concentrated solutions, however, continued to lose in weight during successive periods of heating, the total loss being in no case less than 0.50 per cent. Determined in the presence of the same weight of the same kind of impurity the per cents. of potassium chloride calculated from the weight of potassium platinichloride dried at 100° C. are considerably higher when the solution was concentrated than

<sup>1</sup> A solution of one part of ammonium chloride in five parts of water which has been saturated in the cold with potassium platinichloride.

TABLE IV.

DETERMINATIONS OF POTASSIUM CHLORIDE IN DILUTE AND CONCENTRATED SOLUTIONS IN THE PRESENCE OF OTHER SALTS AND SULPHURIC ACID.

(The figures show the quantity of potassium chloride obtained, expressed in per cents. of the quantity taken. Weight  $K_2PtCl_6 \times 0.3056 = \text{weight KCl.}$ )

$K_2PtCl_6$ dried at—	Hours of drying.	KCl with no admixture.		KCl with 0.4 gram NaCl.		KCl with 0.2 gram NaCl.		KCl with 0.6 gram $MgSO_4$ .		KCl with 1 gram $H_2SO_4$ .	
		No. 31.	No. 32.	No. 33.	No. 34.	No. 35.	No. 36.	No. 37.	No. 38.	No. 39.	No. 40.
100° C.	2	0.5331 gram KCl in 50 cc. $H_2O$ taken.	0.5452 gram KCl in 4 cc. $H_2O$ taken.	0.2416 gram KCl in 25 cc. $H_2O$ taken.	0.2605 gram KCl in 2 cc. $H_2O$ taken.	0.3768 gram KCl in 37 cc. $H_2O$ taken.	0.3919 gram KCl in 3 cc. $H_2O$ taken.	0.4764 gram KCl in 50 cc. $H_2O$ taken.	0.4861 gram KCl in 4 cc. $H_2O$ taken.	0.4734 gram KCl in 50 cc. $H_2O$ taken.	0.4637 gram KCl in 4 cc. $H_2O$ taken.
	3	99.71	100.34	99.30	100.17	99.57	100.22	99.36	99.73	99.73	100.50
	8	99.71	100.21	99.29	100.07	99.57	100.07	99.45	99.67	99.73	100.42
	11	99.70	100.17	99.29	99.98	99.57	100.03	99.45	99.65	99.73	100.40
	14	99.70	100.11	99.27	99.92	99.57	99.95	99.45	99.64	99.73	100.32
	17	99.70	100.08	99.27	99.90	99.56	99.93	99.44	99.63	99.72	100.31
	20	99.70	100.08	99.27	99.90	99.56	99.93	99.44	99.63	99.72	100.31
	26	99.68	99.94	99.25	99.77	99.56	99.80	99.43	99.52	99.72	100.14
	12	99.68	99.91	99.25	99.74	99.55	99.75	99.43	99.46	99.72	100.11
	18	99.67	99.89	99.25	99.71	99.55	99.70	99.43	99.45	99.72	100.09
130° C.	30	99.67	99.86	99.25	99.69	99.55	99.67	99.43	99.42	99.72	100.07
	36	99.67	99.86	99.25	99.62	99.55	99.61	99.41	99.36	99.69	100.00
	6	99.65	99.79	99.24	99.62	99.54	99.56	99.41	99.36	99.69	99.93
	18	99.65	99.72	99.24	99.56	99.52	99.56	99.41	99.38	99.68	99.86
	30	99.65	99.66	99.24	99.55	99.51	99.52	99.41	99.38	99.68	99.86
	42	99.65	99.63	99.24	99.54	99.51	99.50	99.41	99.30	99.68	99.81
160° C.	6	99.65	99.63	99.24	99.54	99.51	99.50	99.41	99.30	99.68	99.81
	18	99.65	99.63	99.24	99.54	99.51	99.50	99.41	99.30	99.68	99.81
Total loss exclusive of that during first 2 hours at 100		0.06	0.71	0.06	0.63	0.06	0.72	0.05	0.53	0.05	0.69

when it was dilute, but calculated from the weights after drying at 160° C. they are about the same.

Experiments Nos. 39 and 40 are practically equivalent to determinations on potassium sulphate with the addition of hydrochloric and sulphuric acids, the amount of the latter acid being about double that necessary to combine with the potassium to form the sulphate. Since in these experiments the results were practically the same as when no sulphuric acid was added, it is reasonable to assume that the effect of the dilution of the solution is the same whether the potash exists as chloride or sulphate.

In both dilute and concentrated solutions the results obtained in the presence of sodium chloride or magnesium sulphate, were lower than when determinations were made on potassium chloride with no admixture, or with only sulphuric acid.

In the presence of sodium chloride this was due partly, if not entirely, to the smaller quantity of potassium chloride taken. Since about the same amount of alcohol was used in all cases, the percentage error due to solubility of potassium platinichloride in alcohol would be greater, the smaller the quantity of the salt taken, although the actual weight lost might be the same.

In the two experiments where magnesium sulphate was present, the washing with Gladding's reagent and the second washing with alcohol undoubtedly increased the minus errors. Possibly the mere presence of sodium and magnesium salts depresses the results. The fact that the results are lower does not impair their value for the present purpose, as in each case the experiments with the same admixture were both made on nearly the same weight of potassium chloride and in exactly the same manner, except as regards the dilution of the solution.

*Results of Fresenius.*—R. Fresenius<sup>1</sup> in an article published in 1877 describing his method for determining potash as potassium platinichloride, directs to add platinum solution to a *concentrated* solution of the potash salt, wash with *eighty per cent. (by volume) alcohol*, and dry the potassium platinichloride to constant weight at 130° C.

In a later article<sup>2</sup> he gives the following results obtained by this

<sup>1</sup> *Ztschr. anal. Chem.*, 16, 63.

<sup>2</sup> *Ztschr. anal. Chem.*, 21, 238.



method on pure potassium chloride, with and without the addition of sodium chloride, using the factor 0.3056. He states that the potassium platinichloride was obtained in the form of a *fine powder*.

TABLE V.

RESULTS OF R. FRESENIUS ON POTASSIUM CHLORIDE WITH AND WITHOUT ADDITION OF SODIUM CHLORIDE.

(The figures show the quantity of Potassium Chloride obtained, expressed in per cents. of the quantity taken.  $Wt. K_2PtCl_6 \times 0.3056 = \text{weight } KCl$ .)

Hours dried at 130°.	1.0378 gram KCl taken.	0.9563 gram KCl taken.	Hours dried at 130°.	0.0490 gram KCl and 0.1189 gram NaCl taken.	0.6812 gram KCl and 0.4524 gram NaCl taken.
2	100.67	100.42	5	100.19	100.13
7	100.40	100.16	8	100.11	100.06
12	100.23	100.04	11	100.04	99.98
21	100.19	100.00	14	100.02	99.97
30	100.10	99.93	20	100.00	99.94

The results of Fresenius without addition of sodium chloride are corroborated by my results in experiments Nos. 29 and 30 in Table I, and No. 32 in Table IV. In experiments Nos. 19 to 29, Table I, the results are a little higher, due to the lesser solubility of potassium platinichloride in ninety-five per cent. alcohol. The results given in Table IV, where sodium chloride was present, are somewhat lower than those of Fresenius, owing probably to the smaller weights of potassium chloride taken. If the factor, based on the latter and now generally accepted atomic weight of platinum as determined by Seubert, had been used, the results would be 0.42 per cent. higher.

There must be then some considerable plus error which more than compensates for the errors due to the solubility of the salt in alcohol and the use of the wrong atomic weight of platinum. This error is largely attributable to the presence of water in the potassium platinichloride.

Seubert<sup>1</sup> finds that it is difficult to so prepare this salt that it will be free from "*verknisterungs wasser*," which is not completely removed even at 160° C. The slow drying of the pulverulent potassium platinichloride at 100° C., and the further loss in weight after subsequent drying at 130° C. is in harmony with Seubert's experience. The results after drying for many hours

<sup>1</sup> Ann. Chem., 207, 1.

at 130° C. are very close to theory, where eighty per cent. alcohol was used, notwithstanding the solubility of the salt, and are higher if the alcohol were ninety-five per cent.

*Microscopic Examination of the Potassium Platinichloride.*—It has been already stated that the potassium platinic salt, when deposited on evaporation of dilute solutions, was coarsely crystalline, while obtained from concentrated solutions, it was finely pulverulent. Examined under the microscope, the difference was even more striking. The coarse form was found to consist of octahedrons, generally attached to one another, forming thin plates, and corresponded to the descriptions usually given in the books, but when the salt was pulverulent, it consisted largely of curious radiating crystals, a characteristic form consisting of three bars intersecting at right angles to each other. Resting on three of the six arms, they presented at first sight, the appearance of stars with six arms in the same place, but by careful focussing, their true form was revealed.

Prof. S. L. Penfield, of Yale University, has very kindly examined my precipitates, and reports as follows :

Both forms of crystals belong to the isometric system. The coarse crystals being deposited slowly, are normal octahedrons ; the pulverulent crystals, however, owing to their rapid formation, are very much distorted being developed into rods, crossing at 90°, parallel to the direction of the isometric axes.

In both the octahedrons and the interpenetrating rods, there were globular cavities which, before drying, were undoubtedly filled with mother-liquor. Only an occasional cavity could be seen in the octahedrons, but in the rods they were very abundant.

Even after the long continued heating at 130° C. ocular proof was secured that the octahedrons were not entirely dry. Patient search revealed the presence of minute cavities from 0.003 to 0.01 mm. across, which were still partially filled with liquid. On inclining the stage about 45° and revolving it about its center, a bubble could be seen to move from one side to the other exactly as the bubble moves in a spirit level.

The facts disclosed by Prof. Penfield's examination, explain the slow drying in my experiments. The octahedrons, being comparatively free from inclosed liquid, did not lose greatly in

weight on heating; the interpenetrating rods, however, contained a very considerable amount of inclosed liquid, part of which was slowly given off on heating at  $100^{\circ}$ , more at  $130^{\circ}$ , and still more at  $160^{\circ}$  C.

The quantity of liquid enclosed in the octahedrons could not have been considerable, but it shows the persistence with which water, once enclosed, is retained.

*Conclusions.*—The method of precipitating in concentrated solutions, and drying the potassium platinichloride at  $130^{\circ}$  depends, for its accuracy, on the compensation of three errors, due (1) to the solubility of the potassium platonic salt in eighty per cent. alcohol, (2) to the presence of water in the crystals which is not driven off at  $130^{\circ}$ , and (3) to the use of a factor based on the wrong atomic weight of platinum. Such a method is certainly open to criticism. The solubility in alcohol occasions an error that can hardly be avoided. It could be diminished by using ninety-five per cent. alcohol, but further experiments would be necessary in order to ascertain whether for other reasons the stronger alcohol could be advantageously substituted for the weaker.

The results given herewith show that *the error occasioned by the presence of water can be greatly reduced and the process of drying simplified, by adding the platinum solution to a dilute solution of the potash salt (one part of potassium chloride or six-tenths part potassium oxide to 100 cc. of water) and drying the potassium platinichloride at  $100^{\circ}$  C.* It is not claimed that the double salt thus obtained is perfectly dry, but it is necessary to heat the pulverulent form for many hours at  $160^{\circ}$  C. in order to secure it as free from water as the granular crystals obtained by the above simple process.

The liquid enclosed in the crystals, although largely water, must contain also solid matters, which remain behind, however complete may be the drying. It must then follow that the less liquid inclosed at the outset, the smaller the error due to this cause after drying.

With such a simple method at our disposal for obtaining the potassium platonic salt comparatively free from moisture, the necessity for using an erroneous factor at once disappears.

The factors based on the atomic weights as revised by F. W.

Clarke<sup>1</sup>, up to January 1, 1894, would be 0.30688 for potassium chloride, and 0.1939 for potassium oxide. These factors would make all the foregoing results 0.42 per cent. higher in potassium chloride, which is equivalent to 0.26 per cent. higher in potassium oxide.

In Table VI are given comparative results by the old and new factors, in the cases of all the preceding experiments in which one part of potassium chloride was dissolved in approximately 100 parts of water, and the potassium platinichloride was washed with eighty per cent. alcohol and dried two or three hours at 100° C.

TABLE VI.

COMPARISON OF RESULTS OBTAINED BY THE FACTORS 0.3056 AND 0.30688 FOR CALCULATING POTASSIUM CHLORIDE FROM POTASSIUM PLATINICHLORIDE.

(Chloroplatinic Acid added to Dilute Solutions of Potassium Chloride, Potassium Platinichloride washed with eighty per cent. Alcohol and dried two to three hours at 100° C.)

Expt. No.	Material taken.	Per cent. KCl found using factor.	
		0.3056	0.30688
9	0.4500 gram KCl.....	99.77	100.19
10	0.5005 gram KCl.....	99.76	100.18
31	0.5331 gram KCl.....	99.71	100.13
33	0.2416 gram KCl and 0.4 gram NaCl .....	99.30	99.72
35	0.3768 gram KCl and 0.2 gram NaCl.....	99.57	99.99
37	0.4764 gram KCl and 0.6 gram MgSO <sub>4</sub> .....	99.26	99.68
39	0.4734 gram KCl and 1.0 gram H <sub>2</sub> SO <sub>4</sub> .....	99.73	100.15

It will be seen that when potassium chloride, either alone, or mixed with sulphuric acid was taken, the results using the factor 0.30688 are 0.13 to 0.19 per cent. above theory. This would indicate either that the water remaining in the double salt after drying for two or three hours at 100° C. a little more than compensated for the solubility in alcohol, or else that there are other slight plus errors.

When, however, other salts are present, and particularly if

<sup>1</sup> U. S. Dept. Agr., Chem. Div., Bull. 43, p. 340.

Potassium = 39.11.

Platinum = 195.00.

Oxygen = 16.00

Chlorine = 35.45.

the Gladding method were followed, the tendency is toward lower results.

Taken as a whole the new factor gave, in these instances, more satisfactory results than the old factor.

A method which so reduces the error due to inclosed water in the double salt, that it about compensates for the solubility in alcohol, and which employs the factor based on the revised atomic weights, is, in my opinion, to be preferred to one which depends, for the accuracy of results, on the compensation of three errors, one of which is due to the use of a factor known to be incorrect, especially when the former method gives more concordant results and is more readily carried out.

*Summary.*—When chloroplatinic acid was added to a concentrated solution of potassium chloride, a large part of the potassium platinichloride formed was precipitated at once in a pulverulent form, the remainder being deposited on evaporation. After treating with alcohol, filtering, and drying, the double salt was in a fine powder which, examined under the microscope, was found to consist largely of radiating crystals, a characteristic form having six arms, formed by the intersection at right angles of three bars. Numerous globular cavities in the crystals gave evidence that during their rapid formation mother-liquor was enclosed. Owing to this enclosed liquid the double salt dried slowly at  $100^{\circ}$ , lost further in weight after heating subsequently for many hours at  $130^{\circ}$ , and further still at  $160^{\circ}$  C. The loss at these temperatures compared with the weight after drying three hours at  $100^{\circ}$ , was equivalent to about six-tenths per cent. potassium chloride.

When, however, the solution of the potash salt was so dilute that no precipitate was formed on adding the reagent, the potassium platinic salt being deposited on evaporation, the latter was obtained in octahedrons, generally attached to one another forming crystalline plates. These octahedrons were comparatively free from cavities, and practically the same results were secured after drying three hours at  $100^{\circ}$ , as after drying for many hours at  $130^{\circ}$  and  $160^{\circ}$  C.

Somewhat lower results were obtained in the presence of sodium chloride and magnesium sulphate, whatever the dilution of the

solution, but in other respects the above statements will hold true.

The kind of dish used, the temperature of the evaporation, the presence of free hydrochloric acid and free sulphuric acid, did not appear to influence the results.

A method based on the evaporation of dilute solutions, drying the potassium platinichloride at  $100^{\circ}$ , and the use of the factors 0.30688 for potassium chloride and 0.1939 for potassium oxide, gave good results and is believed to be more satisfactory for scientific and practical reasons, than the method of Fresenius, in which the platinum solution is added to concentrated solutions, the double salt is dried many hours at  $130^{\circ}$  C. and the factors 0.3056 and 0.19308 are used.

### THE INDIRECT ANALYSIS OF MIXTURES CONTAINING A COMMON CONSTITUENT.

BY EDWARD K. LANDIS.

Received March 15, 1895.

#### FIRST METHOD.

**C**ALCULATION of mixtures containing a common constituent.

*Data given:*

Weight of mixture.

Weight of common constituent in mixture.

Let  $x$  = one salt.

Let  $y$  = the other.

Let  $a$  = amount of common constituent in one part of  $x$ .

Let  $b$  = amount of common constituent in one part of  $y$ .

Let  $z$  = weight of mixture.

Let  $Q$  = weight of common constituent in mixture.

To find values of  $x$  and  $y$ :

$$x + y = z.$$

$$ax + by = Q.$$

$$a(z - y) + by = Q.$$

$$az - ay + by = Q.$$

$$by - ay = Q - az.$$

$$y = \frac{Q - az}{b - a} \text{ and } x = z - y.$$

## SECOND METHOD.

Same data. Calculate the weight of salt of greatest molecular weight if entire amount of common constituent were combined with it. Subtract from this the weight of the mixture. This difference is proportional to the amount of salt of least molecular weight contained in the mixture. Therefore, form the proportion

$$\left( \begin{array}{c} \text{Molecular weight} \\ \text{heaviest} \end{array} \right) - \left( \begin{array}{c} \text{Molecular weight} \\ \text{lightest} \end{array} \right) : \left( \begin{array}{c} \text{Difference.} \\ \text{found above} \end{array} \right) \\ :: \left( \begin{array}{c} \text{Molecular weight} \\ \text{lightest} \end{array} \right) : x.$$

$x$  = amount of salt of least molecular weight contained in the mixture.

## INDIRECT ANALYSIS.

*Example. Method No. 1.*—A sample of  $\text{NaHCO}_3$ , containing  $\text{Na}_2\text{CO}_3$ , gave 97.21 per cent. of the mixed carbonates, and 50.98 per cent of  $\text{CO}_2$ .

$$\text{NaHCO}_3 = 0.5238095 \text{ CO}_2.$$

$$\text{Na}_2\text{CO}_3 = 0.4150943 \text{ CO}_2.$$

$$\text{Let } x = \text{per cent. NaHCO}_3.$$

$$\text{Let } y = \text{per cent. Na}_2\text{CO}_3.$$

$$\text{Then } a = 0.5238095.$$

$$b = 0.4150943.$$

$$z = 97.71.$$

$$Q = 50.98.$$

$$x + y = 97.71.$$

$$x = (97.71 - y).$$

$$0.5238095x + 0.4150943y = 50.98.$$

$$0.5238095(97.71 - y) + 0.4150943y = 50.98.$$

$$51.1814 - 0.5238095y + 0.4150943y = 50.98.$$

$$0.1087152y = 0.2014.$$

$$y = 1.85254 = \text{per cent. Na}_2\text{CO}_3.$$

$$x = 95.85746 = \text{per cent. NaHCO}_3.$$

Proof:

$$\begin{array}{r} 1.85254 \times 0.4150943 = 0.76897 \\ 95.85746 \times 0.5238095 = 50.21104 \\ \hline 50.98001 \end{array}$$

*Example. Method No. 2.*—Same data as before.

Molecular weight.		Molecular weight.	Amount NaHCO <sub>3</sub> .
CO <sub>2</sub> : per cent. CO <sub>2</sub> found = NaHCO <sub>3</sub> : $x$ .			
44:	50.98	= 84	: 97.3255.
97.71 — 97.3255 = 0.3845.			

$$\left( \begin{array}{c} \text{Molecular weight} \\ \text{Na}_2\text{CO}_3 \end{array} \right) - \left( \begin{array}{c} \text{Molecular weight} \\ \text{NaHCO}_3 \end{array} \right) : \left( \begin{array}{c} \text{Difference} \\ \text{found} \end{array} \right)$$

$$= \left( \begin{array}{c} \text{Molecular weight} \\ \text{Na}_2\text{CO}_3 \end{array} \right) : \left( \begin{array}{c} \text{Per cent. Na}_2\text{CO}_3 \\ x \end{array} \right)$$

$$22 : 0.3845 = 106 : 1.852.$$

$$\text{Na}_2\text{CO}_3 = 1.852 \text{ per cent.}$$

$$\text{NaHCO}_3 = 95.858 \text{ per cent.}$$

Proof:

$$\begin{array}{r} 1.852 \times 0.4150943 = 0.76875 \\ 95.858 \times 0.5238095 = 50.21133 \\ \hline 50.98008 \end{array}$$

### ACCURACY OF THE DYEING TEST.

BY CHARLES S. BOYER.

Received April 8, 1895.

THE accuracy and value of the laboratory dyeing test of the natural organic dyestuffs, such as logwood, etc., is a much mooted question among those engaged in the dye-stuff trade. Some hold that the dyeing test is only of value where the dyestuff is to be used in exactly the same manner as the laboratory test, and since about every dyer has his own modifications of the general method of dyeing with the dye-stuff the test is useless except for special cases. Still others hold that the dyeing test never gives the actual value of the dyestuff.

To ascertain the accuracy of the dyeing test the writer made a series of comparative dyeing tests, and also analyzed the dyestuffs according to the best methods of analytical chemistry now known. For these tests several samples of logwood and extract of sumac were used.

*Logwood.*—Fifty grams each of two different samples of thoroughly dried chipped "St. Marc" logwood were repeatedly extracted with water and the weak liquor evaporated to one



liter, care being taken to remove all insoluble matter from the solution. A number of skeins of worsted yarn, of five grams each, were mordanted in separate baths containing 0.150 gram potassium bichromate and 0.075 gram potassium tartrate in 500 cc. water. Two of these skeins were dyed respectively in baths containing thirty-five cc. of each extract, when it was found that sample No. 1 was considerably stronger than No. 2. Dyeing tests were now made, using varying amounts of No. 2 and thirty-five cc. of No. 1, with the result that thirty-five cc. of the latter were equal to forty-five cc. of No. 2, from which we find that 100 parts No. 1 equal, in tinctorial value, 128.5 parts No. 2.

One hundred cc. of each extract solution were now filtered through thoroughly washed hide powder, as described by L. Schreiner (*Chem. Ztg.*, 1890, 961), and the filtrate evaporated to dryness and dried at 100° C. until constant weight is obtained. One hundred cc. of each of the original solutions were also evaporated to dryness and dried at 100° C., the difference in the weights being the coloring matter removed. The results were:

	No. 1. Gram.	No. 2. Gram.
Weight of residue from 100 cc. of the original solution after evaporating to dryness.....	0.6110	0.4714
Weight of the dry residue from 100 cc. of the original solution after being filtered through hide powder.....	0.0368	0.0313
Weight of coloring matter.....	0.5742	0.4401

from which we find that 100 parts No. 1 equal, in tinctorial value, 130.4 parts No. 2.

Another experiment was made to ascertain the accuracy of the Schreiner method, using a sample of hematein which had been made by the writer from chipped logwood.

Five grams of this pure, powdered, and dried hematein were dissolved in one liter of water and 100 cc. of the solution run through hide powder, and the filtrate evaporated to dryness.

Results:

- (1) Hide powder removed from 100 cc. of original solution, 0.4989 gram. Theory, 0.5000 gram.
- (2) Hide powder removed from 100 cc. of original solution, 0.4991 gram. Theory, 0.5000 gram.

This shows that hide powder will remove practically all of the coloring matter of logwood.

It may be well to mention just here, that while the Schreiner method is accurate when working on pure extracts and chipped woods, it is absolutely worthless so far as giving the percentage of hematein and hematoxylon in extracts adulterated with quercitron bark, tannin-containing compounds, etc.

The hide powder treatment extracted 0.965 gram of matter from 100 cc. of a fifty per cent. hematein and fifty per cent. tannin solution, while theory required but 0.500 gram of hematein.

Trimble's volumetric method of the color reaction given by two samples, when treated with copper sulphate, gave a dilution of 100 cc. for No. 2 to 127 cc. for No. 1, which indicates that 100 parts No. 1 are equal to 127 parts No. 2.

The above results show that a dyeing test, when applied to chipped logwoods and unadulterated extracts of logwood, yield results that will compare favorably with most of the methods used in analytical chemistry.

*Extract of Sumac.*—A series of dyeing tests were also made upon six samples of extract of sumac which came to me in the ordinary course of business.

The dyeing tests were made as follows: one and a half grams of each extract were diluted with water to 500 cc., and then a five gram skein of "boiled out" cotton yarn was "laid down" in each bath over night. The temperature of the baths during the night was the ordinary room temperature. The next morning each skein was taken out of the bath and all wrung out as nearly alike as possible. Baths, equal in number to that of the skeins, were made containing two and one-fourth grams of ferrous sulphate to 500 cc. of water, and the skeins "entered" cold and turned for thirty minutes when the solutions were brought to a boil in a water-bath and held there one hour. The skeins are now taken out, rinsed, and dried. After several trials, varying the amount of extract in each bath, it was found that the following amounts gave shades which were of the same depth and intensity:

Sample No. 1657 .....	2.011 grams or 134 parts.				
" " 1661 .....	1.830	"	"	122	"
" " 1662 .....	1.575	"	"	105	"
" " 1663 .....	1.800	"	"	120	"
" " 1665 .....	2.200	"	"	146.7	"
" " 1666 .....	1.500	"	"	100	"

This shows that 100 pounds of No. 1666 will do the same work as 134 pounds of No. 1657, or 146.7 pounds of No. 1665, etc.

Now of each extract four to eight grams were weighed out and dissolved in one liter of water, and the tannin determined in them by the hide powder method as described in Allen's Commercial Organic Analysis, 3, Part I, 119. The results are as follows:

No.	Specific gravity.	Total solids.	Tannin.	Non-tannin.	Relative value in parts.
		Per cent.	Per cent.	Per cent.	
1657.....	1.2445	45.91	18.50	27.41	136.1
1661.....	1.2741	49.51	20.99	28.52	119.9
1662.....	1.2849	51.32	23.48	27.84	107.2
1663.....	1.2648	49.11	21.03	28.08	119.7
1665.....	1.2738	49.14	17.30	31.84	145.5
1666.....	1.2438	45.27	25.18	20.09	100.0

A comparison of these results with those obtained upon the same samples by means of the dyeing test shows a very close and favorable agreement.

While the hide powder method is not all that could be desired in the line of accuracy, yet, in the present knowledge of the chemistry of the tannins, it is the best method we have for the valuation of such extracts as are used on account of their tannin contents. This method also yields results which are much nearer the practical value, and can, in all fairness, be used as the standard in the valuation of extracts by the dyeing test.

The results of the above investigation are: First, the dyeing test yields results which compare favorably in accuracy with the best methods of analytical chemistry. Second, that the results of the dyeing test have a practical value.

Another feature of the dyeing test applied to the natural organic dyestuffs is, that it will frequently show not only any admixture with other dyestuffs, but also give an indication of the method employed in their manufacture. Suppose, for example, one of the extracts of sumac had been adulterated with

extract of quercitron bark. Such an addition would have been indicated by the modification of the shade given with ferrous sulphate. Again, had the extract of logwood been oxidized with hydrogen peroxide, etc., the color would have been taken up by the wool fiber much quicker and the deep blue shade would have developed much sooner than with an extract not so oxidized.

CAMDEN, N. J., April, 6, 1895.

### ABSORBENT BLOCKS.<sup>1</sup>

BY PETER T. AUSTEN AND W. HOMER BROADHURST.

Received April 16, 1895.

FOR drying moist precipitates unglazed plates are generally used in the laboratory, but they have the disadvantages of being rather expensive, as well as fragile, while their absorptive capacity is not great.

We have found that a mixture of equal parts of infusorial earth and plaster of Paris, when moistened, will set, forming a block that after drying has a very strong absorbent power for liquids. The plaster and infusorial earth are thoroughly mixed, then moistened with sufficient water to work easily, and placed in the molds. After setting, the blocks are placed in an air-chamber and heated for a day or two at 100°–120° to free them from hygroscopic moisture.

The molds are easily made in the following way: A sheet of glass, the larger the better, is laid on a table, and rubbed with waste oiled with a few drops of light lubricating oil. Long glass strips, an inch wide, and one-quarter of an inch or more thick, are laid on edge on the plate at a distance apart of six inches, if the block is intended to be of that size, and cross-pieces of the same kind of glass strips, but cut in suitable lengths, are placed between the long parallel strips, thus making squares. The strips should also be oiled a little. The wet mixture is poured in and the top smoothed with a straight edge of wood. After setting, the strips of glass are easily removed and the blocks come off the plate easily, and are ready to be placed in the drying oven. The surface next to the glass plate is very smooth.

<sup>1</sup> Read before the N. Y. Section, March 8, 1895.

These blocks are very convenient in qualitative analysis, and in the preparation of substances. The filter-paper containing the wet precipitate, or substance to be dried, is placed on the smooth side of the block, and after a short time much of its moisture is absorbed. One or more filter-papers may be placed between the substance and the block if too intimate contact of the substance and the block be not desired.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

## THE VOLUMETRIC DETERMINATION OF ZINC AND A NEW INDICATOR FOR FERROCYANIDE.<sup>1</sup>

BY GEORGE C. STONE.

Received March 11, 1895.

**B**EFORE titrating with ferrocyanide it is necessary to separate all the metals of the iron group. Rapid and accurate methods are known for all but manganese; the methods commonly used in gravimetric analysis take too long; and I have been unable to get even passably accurate results on the New Jersey ores by the method of Messrs. von Schultz and Low,<sup>2</sup> or the modification of it proposed by Mr. Hinman.<sup>3</sup> Not finding any satisfactory method of separation I have tried titrating the two together, determining the manganese in a separate portion, by titration with permanganate, and taking the zinc by difference, and find the method easy, rapid, and sufficiently accurate for technical work.

*Indicators.*—Uranium salts are generally used as indicators for ferrocyanide and are fairly satisfactory when titrating zinc alone, though the sensitiveness of the test varies very much with the amount of free acid present. In titrating manganese, uranium cannot be used in the usual manner because it reacts on the precipitated manganese ferrocyanide; good results can be obtained by its use by putting drops of the solutions to be tested, on filter-paper and allowing them to run together so that the uranium does not touch the precipitate; the reaction develops very slowly making the titration very tedious. Ferric chloride, another

<sup>1</sup> Read before the N. Y. Section, March 9, 1895.

<sup>2</sup> Colorado Scientific Society, June 11, 1892; *J. Anal. Appl. Chem.*, 6, 68a.

<sup>3</sup> S. of M. 2, 14, No. 1; *J. Anal. Appl. Chem.*, 6, 682.

commonly used indicator, proved entirely unsuitable. Copper sulphate was found to be about as delicate as uranium, but open to the same objections. Cobalt nitrate was by far the best indicator tried; the delicacy of the reaction is not affected by as much as one part of concentrated hydrochloric acid in fourteen of water; the reaction shows instantly and cobalt does not react on the precipitates. The cobalt solution should be quite dilute; a drop of it is placed on a white porcelain plate, and a drop of the solution to be tested by it, so that the drops touch but do not mix; an immediately shown faint greenish line, at the junction of the two, marks the end reaction. If the drops mix it is impossible to see the reaction; if the color does not show at once the end is not reached. Often when near the end the color will show after standing a few seconds, but at the actual end-point it shows as soon as the drops touch.

Manganese must be titrated at the ordinary temperature of the laboratory; at higher temperatures the amount of ferrocyanide used varies with the temperature. The composition of the precipitate is not normal, but is  $Mn_3Cf_4$ ; that is, an amount of ferrocyanide that will precipitate four atoms of zinc will only precipitate three of manganese.

*Ferrocyanide Solution.*—The best strength was found to be about thirty grams to the liter. It is standardized by titrating solutions containing known amounts of zinc or manganese, using about one-tenth gram, making slightly acid with hydrochloric acid and keeping the solution at about the volume used in the analysis.

The amount of ferrocyanide necessary to give a reaction with cobalt in this volume of acidulated water must be determined, and the amount so found deducted for each titration; it is about seven-tenths cc. for a volume of 140 cc.

*Permanganate Solution.*—1.99 grams of crystallized potassium permanganate to the liter gives a solution, one cc. of which equals 0.001 gram of manganese. It is standardized in the usual manner by iron, and the strength obtained by multiplying the iron value by 0.294646 (ten iron equals three manganese).

Sulphide ores are best dissolved in hydrochloric acid and potassium chlorate, taking care to have sufficient acid present to

keep all the manganese in solution. Oxides, carbonates, and silicates can be dissolved in hydrochloric acid and oxidized by boiling with potassium chlorate. Ores containing franklinite or rhodonite must be fused with sodium carbonate and evaporated to dryness with hydrochloric acid to decompose them thoroughly, then taken up with a slight excess of hydrochloric acid, and boiled with potassium chlorate to oxidize the iron.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminum. Cadmium, if present, must be precipitated by hydrogen sulphide and the solution oxidized after filtering out the precipitate.

Iron and alumina are best separated by barium carbonate; the solution should, preferably, not contain a very large amount of free acid; the iron must all be ferric; the solution must not be warmed and, most important, the barium carbonate must be entirely free from alkaline carbonates and hydroxides, barium hydroxide, and ammonium salts. No barium carbonate in the market answers these requirements, but the ordinary chemically pure salt can easily be purified so that it answers perfectly. Select a salt that is free from ammonia (*e. g.*, Merck's), suspend it in water, and warm for several hours with two or three per cent. of its weight of barium chloride; this converts the alkaline carbonate present to chloride; the small excess of soluble barium salt does not interfere.

The thoroughly oxidized solution of the ore should be washed into a 500 cc. flask, cooled, and barium carbonate, suspended in water, added until the precipitate curdles; an excess of barium does no harm. The change in the appearance of the precipitate is very marked. Pour into a beaker, mix thoroughly, let it settle, decant the clear liquid through a dry filter, and take portions of 50, 100, or 200 cc. for each titration. The solution must be filtered from the iron at once and should be titrated as soon as filtered. If it be necessary to let the solution stand it must be made slightly acid or some zinc will precipitate. One portion, which should contain between 0.01 and 0.04 gram of manganese, is diluted to about 200 cc., heated nearly to boiling in a white porcelain dish, and titrated rapidly with permanganate

with very vigorous stirring. The greater part of the permanganate necessary should be added as rapidly as possible or the manganese oxide is apt to stick to the sides of the dish, making it difficult to see the pink color of the solution at the end. To obtain satisfactory results, the titration must be performed rapidly, so that, if the percentage of manganese be not approximately known, it is better to make a preliminary titration, adding one or two cc. at a time.

In a second portion, made slightly acid<sup>1</sup> with hydrochloric acid, the zinc and manganese are titrated together cold by ferrocyanide; if the manganese be present in appreciable quantity the color of the precipitate will darken as the ferrocyanide is run in and quite suddenly change to a light greenish yellow shortly before the end is reached. It is not necessary to begin to test the solution with cobalt until one or two cc. after the lightening of the precipitate; it should then be tested after the addition of each few drops. If there be little or no manganese present and the percentage of zinc be not approximately known, it saves time to make a preliminary titration, adding one or two cc. at a time. If lead be present the solution must be made quite strongly acid<sup>1</sup> before titrating to prevent the lead from being precipitated as ferrocyanide; five cc. of hydrochloric acid in 100 cc. of solution is sufficient.

The calculation of the results is best shown by an example: One cc. of the ferrocyanide used equaled 0.00606 gram of zinc or 0.00384 gram of manganese; one cc. of the permanganate equaled 0.001 gram of manganese; two and one-half grams of the ore were dissolved and the iron precipitated and filtered out as described above; fifty cc. of the solution was diluted, heated, and titrated with permanganate, requiring 18.45 cc., equal to 7.38 per cent. of manganese. 100 cc. titrated with ferrocyanide required 27.85 cc. The previous titration had shown that there was 0.0369 gram of manganese present which would require 9.61 cc. of ferrocyanide; deducting this left 18.24 cc. for the zinc, equal to 0.11053 gram, or 22.11 per cent.

<sup>1</sup>Manganese ferrocyanide is soluble in a large excess of hydrochloric acid, which should therefore be avoided; or the results will be low if much manganese be present. Five cc. of concentrated hydrochloric acid added to 100 cc. of a solution containing 0.03 gram of manganese did not cause any appreciable error. Ten cc., however, prevented the precipitation of any manganese.



This method has been used for some months in the laboratory of the New Jersey Zinc and Iron Co., with very satisfactory results. The following table shows how this compares with the ordinary gravimetric methods.

Material Analyzed.	Zinc		Manganese	
	Gravimetric.	Volumetric.	Gravimetric.	Volumetric.
N. J. ore.....	22.05	22.11	7.58	7.38
" " .....	26.58	26.48	N. D.	11.98
Brass.....	5.06	5.12	O.	O.
N. J. ore.....	22.50	22.47	N. D.	11.55
" " .....	30.75	30.82	"	7.54
Blende .....	38.28	38.18	"	0.14
Willemite .....	55.55	55.68	O.	O.
Residuum .....	4.60	4.79	12.23	12.30
" .....	4.29	4.44	N. D.	11.99
" .....	9.15	8.99	"	11.61
Tailings .....	2.12	2.05	6.04	6.00
Middles .....	15.15	15.24	9.24	9.14

In conclusion I wish to express my thanks to Mr. D. A. Van Ingen, who has done much of the experimental work necessary in testing the method.

### SOME PHYSICAL ASPECTS OF THE NEW GAS, ARGON. THE IDEAL THERMOMETRICAL SUBSTANCE FOR HIGH TEMPERATURES.

BY W. R. QUINAN.

Received March 31, 1895.

THE discovery, by Lord Rayleigh and Professor Ramsay, of a new gaseous constituent of the atmosphere, has a many-sided bearing upon science and excites the interest of the whole world.

While there may be mooted questions yet to be decided in regard to the elementary constitution of argon, certain extraordinary conclusions seem to have been reached. In the sense of the kinetic theory, it is a monatomic gas; that is, if heat be applied to it, all or very nearly all of this heat will be expended in dynamic energy. The kinetic theory, whatever may be its shortcomings, is certainly the most intelligible hypothesis now at our command, both to explain and to expound the ideal behavior of matter in its simplest form—the gaseous. The behavior, it must be remembered, is independent of the theory. It is the fruit of experimental research.

According to the kinetic theory, in a monatomic gas the ratio of the specific heat under constant pressure to the specific heat at constant volume is one and two thirds. In diatomic gases, some of which are sufficiently normal in their behavior at ordinary temperatures to allow the experimental ratio to be taken as the theoretical—this ratio is about 1.41. In triatomic gases the theoretical ratio is 1.273, and so on according to a relation applicable to all molecules except monatomic

$$\gamma = 1 + \frac{0.41}{\frac{1}{2}N} \quad (a)$$

in which  $\gamma$  is the ratio and  $N$  the number of atoms in the molecule.

The kinetic view is briefly as follows: A gas consists of discrete molecules endowed with energies. Of these, the dynamic energy, referred to the units of space and time, is measured (under the condition of uniform distribution) by the pressure. This is due to the motions of the molecules as entities. But the molecule itself is usually a complex system, consisting of two or more united atoms. The parts of this secondary system are capable of rotation about their center of mass and, perhaps, of various other movements, such as vibrations of the constituent atoms. The energy absorbed by the motions of this secondary system (under the condition of rest for the center of mass) may be called for simplicity the internal energy, while that due to the movement of the molecule as a whole may be called the kinetic. According to the conception and the laws of mechanics, the "free path" of a molecule is rectilinear. By encounters or collisions between the molecules there is a constant exchange and redistribution of the energy between these two forms of energy, but for every gas (in the ideal state) a constant ratio is preserved between the two forms, and each form, therefore, preserves a constant ratio to the whole energy.

In all gases, the ratio  $\beta$  of the whole energy to the kinetic, bears a simple relation to  $\gamma$ , the ratio of the specific heats, as follows:

$$\beta = \frac{2}{3(\gamma - 1)} \quad (b)$$

$$\gamma = 1 + \frac{2}{3\beta} \quad (c)$$

Combining (b) with (a) above we have

$$\beta = \frac{N}{1.23} \quad (d)$$

This formula (d) like (a), from which it is derived, applies to all molecules except monatomic.

In a monatomic gas the only energy which can be absorbed by the molecule (single atom), considered at rest with respect to its center of mass, is one of rotation. On account of the infinitesimal size of the atom this energy is negligible, and for such a gas  $\beta$  may be taken as unity; whence, as from formula (c)  $\gamma = 1\frac{2}{3}$ .

The gases believed to be monatomic by chemists are the vapors of sodium, cadmium, zinc, and mercury. Until the discovery of argon, the only gas for which the relation above had been verified was mercury. Kundt and Warburg showed, by comparing the wave-lengths of the same sound in air and mercury vapor, that  $\gamma$  for the latter was one and two-thirds—an extraordinary confirmation of the bold speculations of Clausius.

Argon has dispelled certain beliefs in regard to monatomic gases. High boiling-points can no longer be regarded as characteristic.

Whatever nomenclature we adopt, whether we accept the ingenious suggestion of Professor Dolbear, in his "Matter, Ether, and Motion," that the internal energy of a gas is to be considered its "heat" proper, or content ourselves with Helmholtz's wider generalization of "free" and "bound" energy, the *fact* is none the less certain, that the energy of gases (monatomic excepted) exists in two distinct forms. In no other simple way can we account for the difference in the action of heat upon them—a difference directly connected in the molecular hypothesis with their complexity of constitution.

The conception of  $\beta$  as well as that of  $\gamma$  is, therefore, founded in fact.

The relations of  $\beta$  and  $\gamma$  are independent of the kinetic conception. To deduce them it is only necessary to supplement the laws of gases with two other laws, both well founded; *viz.*, Avogadro's, that equal volumes of gases under like pressure and temperature contain equal numbers of molecules, and the hypoth-

esis of Clausius that the specific heat of an atom in the (perfect) gaseous state is constant and the same for all elements. This latter hypothesis is the corner-stone of the kinetic theory in which Avogadro's law, as well as the laws of gases, is a rigid deduction.

The theoretical behavior of gases under changes of temperature, pressure, and volume, is regulated by the law of Boyle and the law of Charles. According to the first, at constant temperature the product of the pressure and volume is constant; according to the second, equal volumes of all gases expand equally under constant pressure, or show equal increments of tension at constant volume, for equal increments of temperature.

*These laws are ideal.* No gas obeys them with perfect accuracy under every condition, nor even with approximate accuracy under certain conditions. Nevertheless, they have a reality. Any one familiar with the mathematical theory of "limits" can understand their relation to the behavior of gases. We arrive at the conception of the *perfect gaseous state* in the following simple way:

If we trace the properties of a gaseous substance through a considerable range of temperature, we find that below a certain temperature, even under atmospheric pressure, the substance is a liquid. This is its boiling-point. Above this, for a certain range of temperature, although gaseous under ordinary conditions, it may be condensed into a liquid by increasing the pressure, till at length we reach a temperature above which this is impossible. This is its critical or absolute boiling-point. Above this temperature the substance is a permanent gas, but near it the gas is notably "imperfect." As we raise the temperature above this point the behavior becomes more and more nearly normal. The ideal state for every gas is, therefore, simply a question of its state of removal from the critical temperature.

#### MEASUREMENTS OF HIGH TEMPERATURES.

Temperature is the intensity factor of heat—the thermal form of energy. It is practically measured by the voluminal expansion of a standard substance. In the thermodynamic theory, it is independent of the properties of any particular substance. The absolute values of two temperatures, one higher than the

other, are to each other as the heat taken in, to the heat rejected by a perfect thermodynamic engine (with reversible cycle) working between the two temperatures as limits. The value of the degrees being fixed, this scale of temperature agrees very closely with the scale determined by the air-thermometer. It agrees perfectly with the ideal scale of perfect gases, in which equal increments of temperature correspond to equal increments of heat (mass being constant)—a principle simply expressed by saying that the specific heats are constant.

So far in science the attempts at accurate measures of high temperatures have been indissolubly connected with the increase of volume or tension of elementary gases, such as hydrogen and nitrogen. The regularity of their behavior under ordinary conditions of pressure and temperature has been checked and confirmed in various ways. Since the general effect of increasing the temperature is to correct and improve the isothermals of gases, it has been assumed that this regularity is sustained at high temperatures.

These gases have, however, a fatal theoretical defect when used as thermometrical substances at very high temperatures. Being diatomic a certain part of their energy (about 38.5 per cent.) takes the form of internal energy. This is the form in which we believe the heat exerts its decomposing influence. However this may be, these gases are theoretically subject to a gradual thermolysis or decomposition by heat. A part of the heat being rendered latent and being without effect upon the temperature, equal quantities of heat cease to correspond to equal degrees of temperature. Moreover, since in this dissociation of the molecule the specific volume is doubled, the coefficient of expansion under constant pressure or the coefficient of tension at constant volume, is changed, and the scale of temperature based upon either becomes unreliable.

Now, argon, as a thermometric substance at ordinary temperatures, has about the same properties as nitrogen or oxygen. It is a permanent gas with a low critical point— $-121^{\circ}\text{C}$ . Its behavior under the usual conditions will be very similar to that of the mixture of nitrogen and oxygen we call air; its scale is therefore strictly comparable with that of the air-thermometer.

*At high temperatures it is the ideal thermometric substance.*

Neglecting dissociation, all gases improve in their behavior as the temperature rises; all discrepancies pass into the normal<sup>1</sup> which does not affect the scale of temperature of either the constant-volume or constant-pressure thermometer.

Argon has no internal energy; the decomposing influence of the heat is absent; in other words, being monatomic it cannot suffer dissociation and its behavior as a thermometric substance throughout the range of temperature will be strictly normal. No other substance has such simple heat relations over such a great range of temperature.

These theoretical considerations would seem to show that argon has great possibilities for usefulness in the hands of the skilled experimenter. In its discovery science has been given a new instrument of research. If by its use we can detect in the behavior of an elementary diatomic gas at high temperature, such an aberration as would be accounted for by the dissociation of the molecule, this will go far to confirm the conception of discrete molecules, the tenets of modern chemistry, and the kinetic theory of gases. Unless the molecular theory can make new conquests like these, the onward march of science bids fair to overthrow it. Already serious attacks have been made upon it, two of which have appeared in this JOURNAL, 1893, 430; 1894, 516—the brilliant papers by Prof. Trevor. While Prof. Trevor does not do the theory justice, in fact treats it very cavalierly; he is not the only thinker of the present day who has turned his back upon it. The necessity of reducing the mysterious thing we call *chemical energy* to the reign of law, has led to this estrangement. This form of energy is so obscure that we can apply to it only the most general laws of energetics. We must suppose it to consist of an intensity and a capacity factor, and to be convertible into other energy forms with a constant quantitative relation. But even these simple postulates involve us in difficulties with the molecular hypothesis. Intensity determines action. In order that two bodies may react chemically

<sup>1</sup> The normal discrepancy is as follows: All gases are compressed less under great densities and expand more under extreme rarefaction than required by the law of Boyle  $p v = \text{constant}$ —that is the isothermal is normal except near the extremes of pressure and volume for which the product  $p v$  is too large.

they must differ in chemical intensity. But what is chemical action? According to one view, it is a change in which chemical intensities are equalized, with a conversion of part of the chemical energies concerned into other energy forms; according to the other it is a union of atoms. But how can two things, which we suppose to be exactly alike, unite? Whence comes the difference of intensity? By virtue of what principle is the elementary diatomic molecule formed? If this molecule always preserved its integrity, we could regard its diatomic constitution as an elementary condition, but according to our chemical theories, the molecule in many chemical reactions is subject to division. Nevertheless, whenever the atoms are set free they combine according to the diatomic pattern.

It is thus roughly shown that the later views of chemical energy are not supported by the molecular hypothesis. Which shall we throw overboard for the sake of the other, or may we hope for a view which will embrace, possibly revise, and reconcile both?

## THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.<sup>1</sup>

BY FANNY R. M. HITCHCOCK.

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THE estimation of molybdic and tungstic acids, and their separation from each other have been the subject of many investigations, but notwithstanding the time and care expended the results so far attained are not perfectly satisfactory, particularly as regards their separation. The reactions which take place when either element is tested alone cannot be depended upon when the two are together, each seeming to exert some modifying action on the other.

Several years ago, Smith and Bradbury<sup>2</sup> carried out a series of experiments on the precipitation of these two acids, chiefly with salts of the heavy metals. Their research brought out many new and interesting facts relating to the precipitation and

<sup>1</sup> From the author's thesis presented to the Faculty of Philosophy of the University of Penn'a for the degree of Doctor of Philosophy, 1894.

<sup>2</sup> *J. Anal. Appl. Chem.*, September, 1891.

estimation of each acid separately, but failed to produce anything new in the way of a separation. It was with the hope that, by extending the investigation begun by them, to the action of other precipitants on these acids, additional information might be gathered which would lead to more definite results, that the experiments were undertaken, the results of which are offered in the following pages.

The molybdate solutions used in the work were made up from the sodium molybdate. Analysis showed the salt to be pure and to agree with the formula given,  $\text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O}$ .

The tungstate solutions were prepared from the corresponding tungsten salt,  $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}$ . Analysis showed that traces of silica and ferric iron were present, and molybdenum trioxide was found to the amount of three and one-tenth per cent. This was separated by Pechard's method.<sup>1</sup>

Due allowance has been made in all calculations for the amount of molybdic acid found in the sodium tungstate.

It was found best not to prepare more than 250 cc. of the solution of sodium tungstate at one time, as on standing it gradually affects the flask, the glass being attacked, and a sediment appearing which resembles silica, and is of noticeable amount. The solution of sodium molybdate also attacked the glass, but not so strongly nor so quickly as the sodium tungstate.

#### SODIUM TUNGSTATE AND MANGANESE SULPHATE.

The solution of manganese sulphate used was a saturated one. The solution of sodium tungstate contained 27.8600 grams to the liter, and, if completely precipitated by the manganese sulphate, ten cc. of the solution should yield 0.2871 gram of manganese tungstate,  $\text{MnWO}_4$ .

The precipitates all showed the same character, however varied the conditions under which they were formed, being flocculent at first and becoming slimy on standing. They filtered very slowly and were difficult to wash.

The filtrations were made through asbestos in a Gooch crucible, and the filtrates were all tested for tungstic acid by hydrogen sulphide in ammoniacal solution, the solution being subsequently acidified with hydrochloric acid.

<sup>1</sup> *Compt rend*, 114, 173; *Ztschr. Anorg. Chem.*, 1, 262; this JOURNAL, 15, 1 (1892).



*A. Experiment 1.*—Ten cc. of the sodium tungstate solution were diluted to 250 cc. with distilled water, brought to boiling, and fifty cc. of the manganese sulphate solution added. A voluminous precipitate formed at once, which was allowed to settle, then filtered off, washed with boiling water, dried in an air-bath at 180° C., cooled in a desiccator for three hours, and weighed.

Wt. obtained.	Wt. calculated.	Difference.
0.2310 gram.	0.2871	—0.0561 gram.

The filtrate gave a precipitate of tungsten trisulphide.

*Experiment 2.*—Ten cc. of the sodium tungstate solution were treated as before, but the precipitate was allowed to stand for two days, then filtered cold, and washed with hot water.

Wt. obtained.	Calculated.	Difference.
0.2779 gram.	0.2872	—0.0092

The filtrate gave a precipitate of tungsten trisulphide.

*Experiment 3.*—Ten cc. sodium tungstate solution were treated as before; the precipitate allowed to stand for twelve hours, then filtered cold, and washed with cold water.

Wt. obtained.	Calculated.	Difference.
0.2667 gram.	0.2871	—0.0204

*Experiment 4.*—Ten cc. sodium tungstate solution were treated as before; the precipitate was allowed to stand for twelve hours, then brought to boiling, filtered hot, and washed with a hot solution of ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2110 gram.	0.2871	—0.0693.

*B. Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and five grams of ammonium nitrate added; the whole was then brought to boiling, and fifty cc. of the manganese sulphate solution were added; the precipitate was allowed to subside, filtered off, and washed with water containing ammonium nitrate; the filtrate was perfectly clear.

Wt. obtained.	Calculated.	Difference.
0.2351 gram.	0.2871	—0.0520

*Experiment 2.*—Ten cc. sodium tungstate solution were treated as in *B 1*. The precipitate was allowed to stand over night

before filtering, was filtered cold, and washed with cold water containing ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2393 gram.	0.2871	—0.0478

Both filtrates gave tungsten trisulphide.

*C. Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and eighty cc. of ninety-five per cent. alcohol were added; then fifty cc. manganese sulphate solution. The solution was heated, and the precipitate formed slowly. It was voluminous, white and flocculent, becoming granular on standing; it was filtered off while still hot, washed with thirty-three per cent. alcohol, and ignited at a low temperature.

Wt. obtained.	Calculated.	Difference.
0.2666 gram.	0.2871	—0.0164

*Experiment 2.*—Ten cc. sodium tungstate solution were treated as in *C 1*. The precipitate was allowed to stand for several days before filtering, was filtered cold, and washed with thirty-three per cent. alcohol as before.

Wt. obtained.	Calculated.	Difference.
0.2707 gram.	0.2871	—0.0205

A brief inspection of the analytical results given in detail above shows beyond reasonable doubt that the precipitation of tungstic acid from its salts cannot be well hoped for when manganese salts are used as the precipitants. The most varying conditions failing to give any promise of even approximate success, further experiments with manganese salts were abandoned, and attention was turned to uranium salts. Trials were made with uranium acetate, uranyl nitrate, and uranyl chloride. With uranium acetate no precipitate formed in an aqueous solution of sodium tungstate, whether cold or hot, and an excess of either the tungstate or the acetate produced no effect. The addition of a few drops of acetic acid caused no change. Alcohol produced a slight opalescence, but though the solution stood for several days no precipitate formed. When uranyl nitrate was used a precipitate formed at once, which was pale yellow in color, flocculent, and quick to subside. The precipitation seemed to take place equally well in the presence of alcohol, and in that of ammonium salts.

The solution of sodium tungstate used contained five grams in a liter, and ten cc. would therefore yield  $0.0883 +$  gram of uranyl tungstate, if completely precipitated. The atomic mass of uranium was taken as 239.6.

A. Twenty cc. sodium tungstate solution were diluted with twenty cc. of distilled water and five cc. of a solution of uranyl nitrate added, the latter being in slight excess. This was followed by twenty-five cc. of a saturated solution of ammonium chloride, and the whole heated nearly to boiling for two hours, after which the precipitate was filtered off and washed first with water containing ammonium chloride, then with pure water. The filtration was made through Schleicher & Schull's 590 filter-paper, and the precipitate was ignited strongly with free access of air.

Wt. obtained.	Calculated.	Difference.
0.1728 gram.	0.1767	0.0039

The filtrate gave no trace of tungsten trisulphide when tested with hydrogen sulphide, and from the appearance of the precipitate after ignition some reduction had evidently taken place.

B. Twenty cc. sodium tungstate solution diluted with twenty-five cc. distilled water, were precipitated with five cc. of the uranyl nitrate solution. The precipitate was allowed to stand for one hour, was then filtered in the cold, and washed with cold water, on a tared filter which had been dried at  $150^{\circ}\text{C}$ . The precipitate was dried at the same temperature in an air-bath for two hours, and weighed at constant weight.

Wt. obtained.	Calculated.	Difference.
0.1770 gram.	0.1767	+ 0.0003

The filtrate, when tested, gave no trace of tungsten trisulphide. It may be added that when the ammonium chloride used in the first experiment was replaced by alcohol, the precipitation seemed to be equally complete, as there was no evidence of the presence of tungsten when the filtrate was tested with hydrogen sulphide.

To ascertain whether the tungstic acid could be determined volumetrically, the following experiment was made:

A solution was prepared containing fourteen grams of uranyl nitrate in one liter of water. Twenty cc. sodium tungstate solu-

tion were diluted with twenty-five cc. distilled water, and the nitrate solution introduced from a burette, the tungstate solution being constantly stirred, and the end-reaction ascertained by testing with potassium ferrocyanide on a porcelain plate.

Toward the last the reaction is rather slow, so that a brown color may be obtained with the potassium ferrocyanide before the tungsten is fully precipitated. If, however, the solution be allowed to stand a few seconds after each addition of the uranyl nitrate solution, no coloration is obtained on testing, unless the reaction is complete. By a little care the end-reaction can be made extremely close. Upon substituting a solution of uranyl chloride for the nitrate, equally good results were obtained.

#### SODIUM MOLYBDATE AND URANIUM SALTS.

A solution was prepared containing 8.51 grams of sodium molybdate to the liter, and the same salts of uranium were tried that had been used in the experiments with tungstic acid.

With uranium acetate, sodium molybdate behaved similarly to sodium tungstate, no precipitate being obtained by any method tried. With the nitrate of uranium, however, a precipitate is formed at once which redissolves on stirring, though not completely, a small quantity of some flocculent material remaining undissolved; boiling did not bring down any further precipitate, and an excess of the nitrate had no effect. The uranyl nitrate solution was the same as that used with sodium tungstate, and contained fourteen grams to the liter. On trying a concentrated solution of uranyl nitrate a dense precipitate formed at once, which, on dilution, dissolved in part, but very imperfectly.

Addition of alcohol does not change the behavior in either a cold or a hot solution.

A solution containing twenty-five cc. of a saturated solution of ammonium chloride, twenty cc. of the sodium molybdate solution, and twenty-five cc. of water gave no permanent precipitate with uranyl nitrate, but when twenty cc. of the sodium molybdate solution were diluted with twenty-five cc. water, and the uranyl nitrate solution added in excess, the addition of ammonium chloride brought down the whole of the molybdenum.

With uranyl chloride, a precipitate was obtained at once,

which, like that produced by uranyl nitrate, redissolved on stirring, as fast as it formed.

On standing, a pale lemon yellow precipitate appeared, which on heating went into solution. With the addition of an excess of uranyl chloride to the cold solution, a precipitate forms similar in appearance to the one just described, but on heating it does not redissolve. Heated for an hour it grows denser, and gradually becomes crystalline. These crystals are insoluble in water, and those which I obtained were washed first by decantation, then on the filter with cold water, dried on the air-bath at  $128^{\circ}$  C. (without any alteration in appearance), and analyzed.

The molybdic acid was determined by heating the salt in a current of hydrogen chloride gas. The  $\text{MoO}_3 \cdot 2\text{HCl}$  came off readily at a low heat, the salt in the boat changing in color from a brilliant golden yellow to a light green, then to a golden brown, and finally to a dark green, almost to a black.

This blackish residue when treated with concentrated hydrochloric acid did not dissolve; with aqua regia it did slowly dissolve to a deep yellow solution from which the uranium was precipitated by ammonium hydroxide; the precipitate after strong ignition had a metallic appearance. It was dissolved in concentrated nitric acid, evaporated to dryness, and gradually heated to a dull red heat. The brownish yellow powder obtained was weighed as uranium trioxide.

A slight loss occurred when the salt was heated in the stream of hydrogen chloride gas. as a little was carried over mechanically, and heated so strongly to the walls of the tube that it could not be removed.

The weight of material taken for analysis was one-tenth of a gram. The weights obtained were as follows:

Molybdenum trioxide = 0.0333 gram = 33.3 per cent.

Uranium trioxide = 0.0620 gram = 62.0 per cent.

These values correspond very closely to the formula  $\text{UO}_2\text{MoO}_4$ , when the radicle  $\text{MoO}_3$  may be regarded as replacing the two chlorine atoms in the uranyl chloride. The theoretical amounts required for this formula are

Molybdenum trioxide = 0.0334 gram = 33.4 per cent.

Uranium trioxide = 0.0666 gram = 66.6 per cent.

Water of crystallization does not seem to be present; one-tenth of a gram of the substance was dried over sulphuric acid for two days, and then in the air-bath for two hours at a temperature of  $128^{\circ}\text{C}$ . The loss in weight was eight-tenths of a milligram. On strong ignition the color changed at first a light green, then to a golden brown, and on cooling became once more bright yellow. By this ignition a loss in weight occurred amounting to nine and three-tenths milligrams; a second ignition caused no further loss.

Both before and after ignition the salt is readily soluble in hydrochloric acid, apparently without decomposition, as no reaction for uranium is given by the solution when tested with potassium ferrocyanide.

The perfect precipitation of tungstic acid by uranyl nitrate from the sodium tungstate solution, and the non-precipitation of molybdic acid by the same reagent, encouraged a hope that a separation of the two acids might be possible through its means.

As potassium ferrocyanide indicated the end reaction so sharply between sodium tungstate and uranyl nitrate, some tests were made with it as an indicator, with solutions of sodium molybdate and uranyl nitrate. Observing the same precautions as before the end reaction was equally sharp. It was observed, however, that the red color imparted to the potassium ferrocyanide by a drop of the molybdate solution as soon as the uranyl nitrate was in excess, gradually disappeared, and was not restored by the further addition of uranyl salts. The conditions were next varied by introducing the potassium ferrocyanide into the molybdate solution instead of making the tests on a porcelain plate as heretofore. Twenty cc. of sodium molybdate were diluted with twenty-five cc. of water, and five cc. of potassium ferrocyanide added. The uranyl nitrate solution was then run in, the red color appearing when 33.3 cc. of the uranyl nitrate had been used; an excess of six or seven cc. were added, and a deep red solution formed, but no precipitate appeared. After standing for two hours the red color had disappeared, and the solution had become yellow. A portion of this was tested with potassium ferrocyanide, but no reaction was obtained for uranium.

The addition of uranyl nitrate to another portion showed no excess of the potassium ferricyanide. On substituting uranyl chloride for the nitrate the red solution was not obtained, but a reddish brown precipitate came down which was much lighter in color than that given by the uranyl salts alone.

Twenty cc. sodium tungstate solution were mixed with five cc. of the sodium molybdate solution, and diluted with twenty-five cc. of water; the uranyl nitrate solution was next run in from a burette, and the end reaction ascertained by potassium ferrocyanide on a porcelain plate. After standing for an hour the precipitate was filtered off in the cold, and washed with thirty-three per cent. alcohol.

It was hoped that the filtrate would contain the molybdenum, but examination showed that the greater part of it had been precipitated with the tungsten.

A second solution was prepared and titrated in the same manner as before; the precipitate with the supernatant fluid was then heated for an hour at a temperature of 60° C., filtered while hot, and washed with hot water containing thirty-three per cent. of alcohol. The molybdic acid was found in both filtrate and precipitate, though more went into the filtrate than in the first case.

On substituting uranyl chloride for the nitrate and repeating the titration, only a slight precipitate of the tungsten formed, the greater part dissolving with the molybdate, as fast as formed.

An excess of uranyl chloride brought down both the tungsten and the molybdenum completely. It was evident that no separation could be hoped for by means of uranium salts. There seems to be a tendency on the part of the members of the chromium sub-group to form compounds with each other which are not readily broken up, and which probably contain complex radicles of as yet unknown constitution. This is very strongly indicated by the behaviour of molybdic acid with uranyl salts, and the failure of the resulting compound to react in solution, for uranium with potassium ferrocyanide.

As the chief object of my investigations was to ascertain the manner in which the rare earths would act with tungstates and

molybdates, these were now taken up and studied in detail. As the quantity at my disposal of any one of the rare earths used, was necessarily very limited the material had to be worked over frequently, and a great deal of time was in consequence consumed by this preparatory work.

#### SODIUM MOLYBDATE AND CERIUM SULPHATE.

The solution of sodium molybdate used contained 13.24 grams to the liter, so that ten cc. of the solution should give 0.1628 gram of cerium molybdate,  $\text{Ce}_2(\text{MoO}_4)_3$ , if fully precipitated. The solution of cerium sulphate used was saturated.

*Experiment 1.*—Five cc. of the sodium molybdate solution were diluted to 150 cc. with distilled water, and ten cc. of the cerium sulphate solution added in the cold. A voluminous, white gelatinous precipitate formed at once. This stood for eighteen hours, when it had become granular in appearance and was yellow in color. It was filtered cold, washed with cold water, ignited and weighed. The theoretical weights are all calculated for the formula  $\text{Ce}_2(\text{MoO}_4)_3$ .

Wt. obtained.	Calculated.	Difference.
0.0760 gram.	0.0814	—0.0054

*Experiment 2.*—Five cc. of the sodium molybdate solution diluted to 150 cc. with distilled water were brought to boiling, when ten cc. of the cerium sulphate solution were added. A white precipitate formed at once, soon becoming curdy, and then granular, the color changing to yellow. This was allowed to stand for twelve hours, was then filtered, and washed with hot water, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.0752 gram.	0.0814	—0.0062

*Experiment 3.*—Ten cc. sodium molybdate solution were diluted to 500 cc. with distilled water, and fifteen cc. of the cerium sulphate solution added in the cold. The precipitate after standing for twelve hours was filtered on asbestos in a Gooch crucible, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1596 gram.	0.1629	—0.0033

*Experiment 4.*—This was a duplicate of No. 3, excepting that the filtration took place as soon as the precipitate had settled.

Wt. obtained.	Calculated.	Difference.
0.1555 gram.	0.1629	—0.0074



From both filtrates additional precipitates were obtained on boiling.

*Experiments 5 and 6.*—Ten cc. of the sodium molybdate solution were diluted to 110 cc. with distilled water and brought to boiling, when fifteen cc. of the cerium sulphate solution were added; after two hours the precipitate was filtered off, washed with hot water, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
5.	0.1496 gram.	0.1629	—0.0133
6.	0.1587 "	0.1629	—0.0042

*Experiment 7.*—Ten cc. sodium molybdate solution were diluted to 110 cc. with distilled water, fifteen cc. of cerium sulphate solution added in the cold, and the whole brought to boiling, when twenty-five cc. of ninety-five per cent. alcohol were added. The precipitate was filtered off through Schleicher and Schull's 590 filter-paper, washed with fifty per cent. alcohol, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
	0.1588 gram.	0.1629	—0.0041

*Experiment 8.*—Ten cc. of sodium molybdate solution were diluted to 110 cc., fifteen cc. of cerium sulphate solution added in the cold, the whole brought to boiling, when one-third the volume of ninety-five per cent. alcohol was added. The precipitate stood for twelve hours before filtering; it was apparently not homogeneous, as a fine white powder was mixed through the yellow cerium molybdate. The filtering was very slow, and the washing with fifty per cent. alcohol was continued for two days.

	Wt. obtained.	Calculated.	Difference.
	0.2118 gram.	0.1629	+0.0489

*Experiment 9.*—Ten cc. sodium molybdate solution were diluted to 100 cc. and fifteen cc. cerium sulphate solution added in the cold, followed by one-third the volume of ninety-five per cent. alcohol. The precipitate was filtered after standing for two hours, and like that in No. 8, was not homogeneous in appearance.

	Wt. obtained.	Calculated.	Difference.
	0.1919 gram.	0.1629	0.0290

*Experiment 10.*—Ten cc. of sodium molybdate solution were diluted to 100 cc., and fifteen cc. cerium sulphate solution added.

The whole was boiled for an hour, allowed to cool, when one-third the volume of ninety-five per cent. alcohol was added. After standing twelve hours, it was filtered, washed with fifty per cent. alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.2156 gram.	0.1629	0.0497

The precipitates from 8, 9 and 10, after ignition, were dissolved in hydrochloric acid, and tested with barium chloride; all gave precipitates of barium sulphate, as was expected. The following experiments were then made to determine what proportion of alcohol could be added without causing the cerium sulphate to precipitate.

a. Five cc. of the cerium sulphate solution were diluted to sixty cc., then twenty cc. of ninety-five per cent. alcohol were added in the cold, and, no precipitate forming, more alcohol was added, five cc. at a time, until seventy cc. in all had been introduced. The solution still remained perfectly clear.

[TO BE CONTINUED.]

## SOME NEW LABORATORY APPARATUS.

BY EDWARD SAUER.

Received January 31, 1895.

### I. HOT AIR MOTOR FOR LABORATORY PURPOSES.

IN laboratories mechanical power is desirable for many undertakings which require continued shaking and stirring of liquids, as well as for rotation and grinding. While the factory steam-engine furnishes usually the necessary power for the laboratory of the technical chemist, nevertheless it is often desirable to have a separate source of power in case, for instance, of this not being in use.

For this purpose the turbines constructed by Raabe<sup>1</sup> have proved themselves useful in certain kinds of work, but only when small power is required. For many purposes the power is too weak, *e. g.*, the shaking of large quantities of liquids and the stirring of thick liquids.

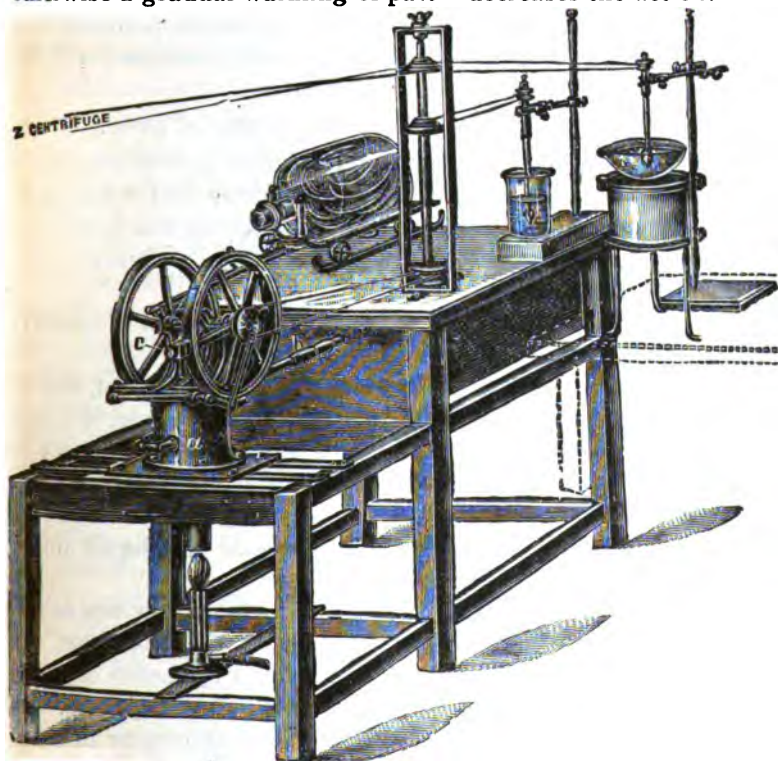
The hot air motor of Heinrici, which is pictured below, and which has already proved of practical value in several labora-

<sup>1</sup> *Ber. d. chem. Ges.*, 1888, p. 1200.

ories, would in most cases furnish abundant power for the different kinds of work.

The motor is built according to the well-known principle of hot air machines, so that its use is absolutely free from danger. It may be heated by gas, petroleum, etc. The more intense the source of heat, the more power the machine furnishes, and if the fire-pot be red hot beneath, the motor furnishes the most power.

About two minutes after the burner heats the pot the motor begins its action. There must be a space of about ten mm. between the burner and pot. A brake upon the fly-wheel regulates the speed of the machine, or brings it to a standstill. While in use, cold water must circulate through the motor, otherwise a gradual warming of part *a* decreases the action.



In the accompanying illustration, the cooling reservoir is

contained in the table, and the circulation of water takes place through the tube *b*. Where a water system is available the body of the motor may be fastened directly in the table by its support.

On the table is fastened a carriage, upon which bottles up to six liters capacity may be shaken vigorously to and fro. The action is most satisfactory with such large quantities.

Should it be desired to shake, at the same time, several bottles of smaller capacity, wooden boxes may be fastened on the carriage which is partitioned and so arranged that each vessel may be easily made firm.

An axle, fastened on the table, receives the belt-cord coming from the motor and is furnished with two movable wheels which furnish connections with Witt's centrifugal stirrers for stirring, evaporating, etc. These stirrers, held as nearly perpendicular as possible in a nickel cylinder, and properly connected with the motor, act in a highly satisfactory manner.

## II. ILLUMINATING APPARATUS AFTER A. LUPP.

This serves for the precise determination of the end-reaction in volumetric analysis, especially in acidimetry and alkalimetry in general, in all quantitative determinations, in which change of color of the indicator (litmus, turmeric, cochineal, etc.) determines the analysis.

The apparatus consists of a tripod, under which a concave mirror is placed at a fixed angle.

By means of this, the sun's rays are concentrated, and so reflected as to pass through the bottom of the beaker, which is placed on the apparatus, through the solution to be titrated to the surface. Since, by means of the apparatus the titration is seen from above, one can, even in *cloudy* weather, always determine exactly the end-reaction because the liquid under examination is always strongly illuminated.

The illuminating apparatus is further adapted to enable one to recognize very fine colored precipitates or colorations, for example, in water analysis reaction for iron by means of potassium ferro- and ferricyanide, and potassium thiocyanate, etc. One needs only to hold a test-tube over the apparatus in order to recognize the slightest trace of a color or precipitate.

## NEW BOOKS.

HANDBUCH DER STEREOCHEMIE. UNTER MITWIRKUNG VON DR. PAUL WALDEN, PROFESSOR DER PHYSIKALISCHEN UND ANALYTISCHEN CHEMIE AM POLYTECHNIKUM ZU RIGA HERAUSGEGEBEN VON DR. C. A. BISCHOFF, PROFESSOR DER ALLGEMEINEN CHEMIE DASSELBST. 1060 Seiten und 250 Abbildungen. Frankfurt am Main: H. Bechhold. 1893-4. Price, 34 m.

In 1880, when the writer of this notice attended the most comprehensive course of lectures on organic chemistry at that time given in America, the lecturer devoted a portion of one hour to the subject of "Physical Isomerism." The theory of the asymmetric carbon atom, proposed almost simultaneously by van 't Hoff and Le Bel in 1874, was alluded to as offering a possible explanation of the opposite rotatory powers and the enantiomorphism of the tartaric acids, and was illustrated by two simple tetrahedral models. Nothing more was said, or could well have been said on the subject. At that time the paradoxical isomerism of fumaric and maleic acids was explained by supposing the latter to contain a carbon atom with free bonds, an assumption totally without experimental justification. Attempts to give structural formulas to the rapidly increasing number of isomers among the crotonic and cinnamic acids and allied bodies resulted only in the worst kind of confusion, and it gradually became evident that either the theory of structure was insufficient or the usual experiments relied on to establish the formulas were worthless. By 1887 a large division of organic chemistry was in an almost chaotic condition. The views of van 't Hoff and Le Bel had received but slight consideration, apparently for no other reason than that chemists had concluded that it was impossible to learn anything about the geometrical arrangement of atoms, and therefore that all attempts to explain phenomena on such hypotheses must be worthless. In this year Wislicenus, who had been one of the few to appreciate the possibilities of a "chemistry in space," published his pamphlet, *Ueber die räumliche Anordnung der Atome in organischen Molekülen*. The appearance of this work marks a point in the development of chemistry of equal or even greater importance than the announcement of the benzene theory by Kekulé; less than eight years have passed, and already the geometry of molecules has become the leading



idea in organic chemistry, to the study of which many of the best workers in the organic field are devoting themselves. How long an idea prematurely born may lie dormant is here well illustrated, Wollaston having in 1808 clearly stated the conception of a tetrahedral arrangement of four atoms about a fifth.

How fruitful the new theory has been, it needs only an inspection of the present book to see. A volume of over a thousand pages is largely devoted to the consideration of isomers which can be explained on the hypothesis of geometrical isomerism, and which cannot be explained on any other which has been proposed, and certainly not on the older conceptions of structure. The remarkable discovery of the isomeric cyclohexane derivatives by von Baeyer, and the brilliant work of Fischer on the carbohydrates are not only the direct offspring of this theory, but would have been impossible without it. One of the most striking evidences of rapid progress is that although the two sections of the *Handbuch* appeared in two successive years, the second has appended a supplement of nearly 200 pages, most of which was required to bring the work up to date.

Although the book is divided into a *general introduction* and a *special part*, the reader would err in supposing the latter to be of importance for the specialist only; it contains quite as much of general and theoretical interest as the former. The *general part* (134 pages) is devoted to an historical review of the subject, and in it may be found about every attempt to explain chemical phenomena by space relations. Of the *special part* the first section (296 pages) is devoted to the relation of stereochemical theories to the optical rotation of organic compounds, with a consideration of nearly all known cases. The proteids are omitted, as their chemical nature is not sufficiently understood. The second section (204 pages) treats of geometrical isomerism in a wider sense, and describes all compounds to which the theory may apply, whether they are at present known in more than one form or not, as well as those which while existing in several forms, cannot be explained by the theory as at present developed. The stereochemistry of nitrogen, as exhibited in the oximes and other bodies is fully treated. Both the older nomenclature and that of the Geneva Congress are used, and the classification is the purely artificial, but extremely convenient one used by Richter in his

*Tabellen der Kohlenstoffverbindungen.* The third section includes a chapter on the formation of rings (124 pages) which while not properly a part of stereochemistry, is valuable as containing a diagram of every kind of ring discovered or supposed to exist, into which carbon enters, as well as many wholly inorganic rings. One wonders what Kolbe would say about the hexa- and hepta-cyclic systems, were he now living. But little is said of the reactions by which these rings are formed, or of the proofs of their structure, but there are full references, which take the place of a broader discussion. This chapter forms a complete "Handbuch der Ringschliessung." Anyone looking up the various benzene theories will find in this work a good directory. The chapter on rings is followed by others on intramolecular transpositions, addition and splitting off of atoms and groups, and the limits of general reactions, in as far as these may be supposed to be influenced by the geometrical structure of the molecule. These constitute one of the most valuable and interesting parts of the work.

The authors are to be commended for having given considerable space to inorganic compounds. Not much was to be said on the subject, as it is still in its infancy; the inorganic ring systems which have an experimental warrant are as yet but few, and these of the simplest nature, and with the exception of a few observations and speculations on sulphur and ammonia derivatives we have yet to see the beginning of a stereochemistry of inorganic bodies. We regard inorganic structure and stereochemistry a promising field for investigators who do not believe that all the laws of chemistry worth knowing can be discovered by the study of carbon compounds only, and who have the courage to strike out in new lines, and the patience to search for new methods. With the view of aiding such pioneers the authors have given in a special chapter a list of inorganic substances occurring in more than one form, which will prove of value to investigators in this field. The list makes no pretension to completeness; we miss, for example, the metaphosphoric acids, some of which may in future prove to be stereoisomers.

A knowledge of stereochemistry has already become essential to a scientific understanding of the carbohydrates, and there are indications that it will play an important part in the chemistry

of fermentation and of the physiological processes. To those who are interested in these branches, as well as to the working organic chemist, and the teacher who is called on to give more than a bare outline of the subject, as well as to every one who wishes to keep up with the development of the science, this work may be heartily recommended.

H. N. STOKES.

**A TEXT-BOOK OF ORGANIC CHEMISTRY.** BY A. BERNTHSEN, PH. D., DIRECTOR OF THE SCIENTIFIC DEPARTMENT IN THE CHIEF LABORATORY OF THE BADEN ANILINE AND ALKALI MANUFACTORY, LUDWIGSHAFEN-AM-RHEIN; FORMERLY PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF HEIDELBERG. TRANSLATED BY GEORGE MCGOWAN, PH. D. pp. 594. New York: D. Van Nostrand Co. 1894. Price, \$2.50.

This book is a translation of the fourth German edition, appearing as the second English edition. The usefulness of Dr. Bernthsen's work is indicated by the fact that the fourth edition is called for within the brief space of six years. A comparison of the former and present editions impresses one with the tremendous activity and rapid development that have been going on recently in this field of chemical research. While this edition follows closely the plan of the previous ones, every part has been carefully revised and several chapters have been entirely rewritten, in order to present the most recent knowledge about the subjects considered. Among such specially revised subjects may be mentioned the following: stereochemical isomerism; the determination of molecular weights by physical methods; aldoximes and ketoximes; carbohydrates; ketonic acids, di-ketones, etc.; special benzene formulas; aromatic compounds of phosphorus, etc.; hydrogenized phthalic acids; dyes of the diphenylene-methane oxide, phenazine, oxazine, and thiazine groups; certain naphthalene derivatives; the quinoline and acridine groups; alkaloids, especially the derivatives of tropine; the terpenes and camphors. The system of international nomenclature adopted at the recent Geneva convention of chemists is used in connection with the former names. The book, as a whole, cannot well be pronounced a comprehensive embodiment of our present knowledge of the essential facts and theories of the organic chemistry of to-day. The author has made a very judicious use of references to original articles which have a historic value. There is a valuable index of nearly thirty pages.



While this book is intended primarily for the use of students, it can hardly be recommended as a desirable work for those just entering upon the study of organic chemistry, since it is much too full for such. It will be found most helpful to those who have such a knowledge of the subject as can be obtained from a work like Remsen's little book on organic chemistry. It will also be a most grateful help to those who are engaged in various lines of chemical work and who desire to keep informed of the present state of knowledge of organic chemistry, but who have not time or means to get their knowledge at first hand from the literature of the various chemical journals.

L. L. VAN SLYKE.

MANUAL OF CHEMISTRY. BY W. SIMON, PH.D., M.D., ETC. Fifth Edition. pp. 502. Lea Bros. & Co. 1895.

Professor Simon has found it desirable to issue a revised edition of what is correctly termed a manual of chemistry. When to the title is added that it is especially a manual for medical students, the experienced reader knows tolerably well what advantages and shortcomings are to be looked for; and if the reviewer adds that the advantages are well represented, and the shortcomings are such as are identical to the plan of the book, it will be easy to form a general idea of its character.

The first fifty pages go over the theory of chemistry from the most elementary definitions to a discussion of the periodic law. Now it is manifestly impossible to give in a couple of hours' reading a satisfactory treatise on such a subject. On the other hand, it is desirable for medical students to have some knowledge of chemical theory; and as the medical student's chemical library consists too often of but one book, it is necessary to put the main facts in that book. It is, of course, understood that the book is to be supplemented by an extended course of lectures, and is intended to give, first, elementary knowledge to the young student, and second, a repository of all the principal things he subsequently learns, for future reference. Now this book gives these things very well indeed; and what has been said of the theoretical part applies to the whole book. It goes into descriptive chemistry, and analysis, qualitative and quantitative, and physiological chemistry, and treats of all the chemicals men-

tioned in the U. S. Pharmacopeia. Happily it was not thought best to include industrial chemistry.

The book is concisely written in good English, and is embellished with eight colored plates, representing sixty-four reactions very useful to the student, and by no means easy to produce; they seem very good.

A. H. SABIN.

### NOTES.

*Note on a Molding-sand.*—A number of years ago a bed of excellent molding-sand was discovered in Belmont County, Ohio, near the Ohio river. It was, in fact, pronounced almost an ideal sand for heavy castings, and so popular was it with foundrymen, that the bed is now about exhausted, and has been closed by the owner.

The sand, when taken from the bed, coheres in lumps, is dark colored and rather coarse-grained. The grains consist of a rounded quartz nucleus, covered with a coating of brownish-red clay, that seems to adhere closely to the quartz, but dissolves when the sand is treated with hydrochloric acid, leaving the pure white nucleus behind.

The sand, even when rammed in a mold, is very porous, readily permitting the escape of gases, it is strongly cohesive, and will not blister or scale off when the molten metal flows over it. Most sands used for making heavy castings soon have the life burnt out of them; but it is said that this sand is wonderfully tough and durable.

Few sands possess, along with other good qualities, this desideratum of life-length.

Whether the good qualities of this particular sand are due to its physical condition, or to its chemical composition, or, as seems likely, to both, the writer cannot say.

An analysis of the sand, dried at 100° C., follows:

Free silica .....	73.47 per cent.
Combined silica.....	5.30 " "
Alumina .....	12.86 " "
Ferric oxide.....	3.97 " "
Lime.....	0.62 " "
Magnesia.....	0.60 " "
Organic and water .....	3.13 " "

Total..... 99.95

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

### THE DECARBONIZATION OF BONE-BLACK.<sup>1</sup>

BY W. D. HORNE, PH.D.

Received April 26, 1895.

THE chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, etc., lies in its power to withdraw from solutions the contained organic coloring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of coloring-matters by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off, and the bone-black subsequently washed with water, naphtha, or other appropriate solvent, to wash out, as far as possible, the coloring-matters, etc., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns, without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high-grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low-grade sugars, and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char about exhausted at the end of

<sup>1</sup> Read before the New York Section, April 12, 1895.

the year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon. When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upward of \$40.00 a ton the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails.

Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world renowned as the inventor of the steam washing centrifugal machine which bears his name. He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet iron, which is heated to a dull red and revolved constantly. The char enters the drum through a central orifice in the head, closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidizes the carbon in the bone-black; that depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, etc.

In case the carbon is all removed the mineral frame-work

remains intact with its pores opened up. This bone-black can then be treated with a solution of glue or molasses, or other carbonaceous matter, to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above recarbonization the grains must be washed with hot water to remove soluble substances; and then the char is ready for use.

In the case of partial decarbonization only one operation, that of passing through the drum, is necessary, where a high carbon char can be reduced to a low carbon char and the process regulated to remove any percentage required.

Washed char, fresh from the filters and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness, which indicates the possibility of this method's replacing the present purification or revivification in kilns.

These methods have been investigated and tested by the author, both in the laboratory and on a working scale, in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavorable results have, at times, appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

#### LABORATORY TESTS ON TOTAL DECARBONIZATION, ETC.

A quantity of old bone-black, discarded from a sugar refinery, and containing in the neighborhood of twenty per cent. of carbon, was heated in the open air until it was burned white. Sufficient low-grade sugar syrup, for its dry substance to be equal to about fifteen per cent. of the weight of the decarbonized char, was diluted with hot water, thoroughly mixed with the burned bone, evaporated to dryness, and the mixture then put into an iron tube, closed at one end, and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonized bone was then cooled



and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about five per cent. carbon. Three hundred cc. of this char were put into a liter bottle with 350 cc. of a solution of molasses sugar, 33° Bé. and exponent = 89.2, and heated one and a half hours in a water-bath at 175° F., with frequent agitations. New char was washed similarly and dried, and 300 cc. subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in color, that from the recarbonized char was considerably lighter than that from the new char. The exponent of the former was 93.0; that of the latter 92.4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. These two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonized char would stand use as well as ordinary char. It was also found that while both samples deteriorated greatly, owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample, at the end, as it had been at the beginning, so far as color was concerned. The new char had increased the exponent 0.17 per cent. more than the treated char, in the average of the nine tests, but while the new char had removed 66.6 per cent. of the color from the average solution the recarbonized char had removed 83.3 per cent.

#### FACTORY TESTS ON A WORKING SCALE.

A decarbonizing apparatus was built, consisting of a cylindrical drum of three-sixteenth inch wrought iron, nine and a half feet long by thirty inches diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed by brickwork and heated by a fire built beneath its lower end. By means of this, either a total or a partial decarbonization of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustment.

Bone-black that had been in constant use nearly a year and containing twelve per cent. of carbon was reduced to nine per cent. of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a color = 200 on an arbitrary scale. The filtrate from the untreated char had a color = 80; that from the treated char had a color = 27.

In another test the original solution had a color of 240.

Filtrate from untreated char.....	110
" " treated char.....	20
" " over-treated char (some white grains) ..	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char,	color = 120
" " treated char,	" = 40
" " over-treated char,	" = .50

In the two treatments the untreated char removed 52.5 per cent. of the color, the treated char 87.9 per cent., and the over-treated char 84.5 per cent.

It was thought that these tests extending over one and a half or two hours might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made. Three hundred cc. of each char were heated at 175°F., with 600 cc. Muscovado sugar solution at 27° Bé. giving the following results:

Original solution had a color = 210

	One and a half hours.	Six hours.
Filtrate from house char.....	50	12
" " new char .....	40	10
" " treated char.....	20	7

showing that the treated char held its own very satisfactorily.

Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonization was made. Three hundred cc. of each black were heated at 175°F. with 600 cc. Muscovado solution of 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average color of the liquor going on was 152.5; that coming off was, house char, 22.8; new char, 16.4; treated char,

16.7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the tests than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonized char over old char, and its equality in many respects to new char.

In the first of these tests a filter of house char containing 12.32 per cent. carbon, and another of decarbonized char containing 10.04 of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a fourth hours. The average liquor from the house char had a color of 25, while that from the treated char had an average color of only 15; and it was very striking that the difference in color increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79.88 per cent. of the color present, while the treated char withdrew 87.69 per cent.

In another set of filtrations on the working scale, in a sugar refinery, a raw sugar solution, color 120 and  $27.7^{\circ}$  Bé., and exponent 90.09, was put, in the regular course of running through filters of char respectively several months old, new, and decarbonized. The average color of that from the old char was 23; from new char, 19; from decarbonized char 18. The exponents scarcely varied, being 92.17, 92.37, and 92.09 respectively.

These are a few of a great many tests both in the laboratory and in the factory made upon char which had been partially decarbonized in a small working model which could not be controlled with the desired nicety. While the average per cent. of carbon in the decarbonized char was 10.04 per cent., or 2.28 per cent. less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than eleven per cent. of carbon, and considerable which had been so over-heated as to be rendered weak as a decolorizer. These two extremes, while giving a favorable-looking average per cent. of carbon, both deteriorate the char for the purposes in hand.



Some improvement having been made in the operation of the decarbonizing drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within half a per cent. of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13.03 per cent. to 10.22 per cent., and two filters filled with these grades were run against each other. The liquor entering had a color of 110. The average of that coming from the untreated char was ten, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only five. From the old char the liquor ran water-white for less than an hour; from the decarbonized char it ran water-white for more than five hours; and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself: after a partial decarbonization, microscopic examination shows the decarbonization to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:

	Before decarbonization.	After decarbonization.
Carbon.....	12.32	8.90
Calcium carbonate.....	3.32	3.26
Iron .....	0.32	0.21
Calcium sulphate.....	0.904	0.877
Calcium sulphide.....	0.628	0.494

The most noticeable and, in fact, the most desirable changes are the reduction of carbon, with a corresponding opening of the pores and increase in absorbing power; and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this latter substance exercises upon the sugar.

Numerous experiments showed that the calcium carbonate is not decomposed by the mild heat which suffices for oxidizing the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis.

The friction of the grains of bone-black against each other in

the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed per cents. of dust as follows :

	Before treatment.	After treatment.
Finer than thirty mesh....	12.56	12.64
“ “ fifty “ ....	0.96	2.20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of specific gravity, probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone-black which, before treatment, had a sp. gr. = 1.0624, and lost 2.81 per cent. of carbon during treatment, had a sp. gr. = 1.0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which, before treatment, gave 1.76 per cent. of dust, by the method described by the author in a previous paper (This JOURNAL, January, 1895), gave 2.84 per cent. after treatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose, who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolorizing power lost ; but he can, by a very simple and inexpensive process, bring it back to its original decolorizing power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition, by submitting it to the decarbonizing process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing instead of charring them as in the ordinary method of revivifying in kilns with the exclusion of air ; and it is not at all impossible that the apparatus will, in the near future, supersede the present kilns used in all factories employing large quantities of bone-black.

YONKERS, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

### SULPHIODIDE OF LEAD.

BY VICTOR LENHER.

Received March 30, 1895.

ACCORDING to Humefeld (*J. prakt. Chem.*, 7, 27) Reinsch (*J. prakt. Chem.*, 13, 130) and Parmentier (*Compt. rend.*, 114, 299) there exists a chloresulphide of lead and an analogous bromsulphide of a cinnabar red color, obtained by adding hydrogen sulphide to a solution of lead chloride in hydrochloric acid, or to the corresponding bromide in hydrobromic acid.

As lead iodide dissolves readily in potassium iodide with the formation of the double iodide  $\text{PbI}_2 \cdot 2\text{KI}$ , and with excess of potassium iodide  $\text{PbI}_2 \cdot 4\text{KI}$ , it was found that when working with this salt an iodosulphide of brick-red color and rapidly changing composition was formed when its solution was treated with hydrogen sulphide.

The precipitate formed, when hydrogen sulphide is added to a solution of the double iodide in potassium iodide, is brick-red in color, rapidly changing, on further addition of that reagent, successively through dark red to brown, and finally the black sulphide is obtained which careful examination showed to be free from iodine. Cold water saturated with hydrogen sulphide was added to a strong solution of lead iodide in a saturated solution of potassium iodide; the red precipitate which was obtained was rapidly filtered by means of a suction apparatus, washed with a saturated solution of potassium iodide to remove any  $\text{PbI}_2 \cdot \text{KI}$  which possibly may have separated by the dilution; it was then washed with cold water till the reaction for iodine entirely disappeared; absolute alcohol was then added to displace the water, followed by carbon bisulphide to remove any sulphur, after which absolute alcohol was again added, and the precipitate dried by drawing cold air over it.

When  $\text{PbI}_2 \cdot 4\text{KI}$  is diluted with water, yellow  $\text{PbI}_2 \cdot \text{KI}$  separates. The red sulphide was examined very carefully for potassium but none was found.

As the tendency of the substance to decompose into lead sulphide and lead iodide was so great, only small quantities were prepared at one time.

The lead was determined by treatment with nitric acid, followed by a few drops of sulphuric, and was weighed as sulphate. The sulphur was determined only after much trouble, as all attempts to oxidize it caused sulphur to separate. The method employed was treatment with a hot solution of sodium carbonate, which completely converted it into lead sulphide, carbonate, and sodium iodide. This was brought upon a Gooch crucible, washed with water, followed by a little dilute acetic acid to remove the carbonate, again washed with water, after which it was treated with nitric and sulphuric acids, and weighed as lead sulphate.

The iodine was estimated by covering the iodosulphide with an excess of a decinormal solution of silver nitrate; decomposition was then effected by means of nitric acid, and the excess of silver titrated with a decinormal ammonium thiocyanate solution, using ferric alum as an indicator. Analysis gave the results:

Lead.	Iodine.	Sulphur.
49.06	49.97	1.51
50.16	49.81	1.98
.....	50.24	2.21
.....	50.33	2.17

The results approximate the composition of  $\text{PbS}_4\text{PbI}_4$ , which requires:

Lead.	Iodine.	Sulphur.
49.20	48.77	1.53

Hydrogen sulphide gas passed through a saturated solution of  $\text{PbI}_4\cdot 4\text{KI}$  in the cold, also gave a brick-red precipitate which treated in the manner described in the previous experiment, gave on analysis, 49.98 per cent. of iodine.

This method for the preparation of the iodosulphide is very unsatisfactory, as it rapidly darkens even in presence of large excess of the iodide, and from the fact that only a small fraction of a per cent. of product can be obtained.

Various colored products were obtained in the investigation

containing lead from 49.06 per cent. to the normal sulphide, and iodine in a similar manner from 50.84 per cent. to a sulphide entirely free from it. All of these but the one approximating,  $\text{PbS}_4\text{PbI}_2$ , were inconstant in composition and more or less rapidly decomposed into lead sulphide and lead iodide, as might be expected from the knowledge of the chlor- and bromsulphides; the iodosulphide is readily decomposed by heat, acids, and alkalies; and even long exposure to light decomposes it.

### ON THE DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE CITRATE METHOD.<sup>1</sup>

BY E. G. RUNYAN AND H. W. WILEY.

Received April 15, 1895.

THE results obtained by analysts in different parts of the world in precipitating phosphoric acid directly by magnesia mixture, in presence of citric acid or its salts, show that this process may safely take the place of the molybdenum method with all standard tricalcium phosphates or their preparations. We have observed in our work the most satisfactory agreement between this method and the molybdenum method of the Association of Official Agricultural Chemists. This statement, however, holds true only when the phosphoric acid is present in considerable quantities, at least in excess of five per cent. With smaller quantities of phosphoric acid we have observed that the citrate method leads to results which are decidedly inferior to those obtained by the molybdenum process.

The principle of the citrate method may be stated as follows: In the presence of a considerable excess of ammonium citrate a solution of a magnesium salt, made alkaline by ammonia, will precipitate the phosphoric acid as ammonium magnesium phosphate. The iron and alumina which may be present in the solution will not be precipitated under the above circumstances either as hydroxides or as phosphates. The ammonium magnesium phosphate can be subsequently separated by filtration, converted into magnesium pyrophosphate and weighed. An examination of the

<sup>1</sup> Read before the Washington Section, April 11, 1895.

pyrophosphate obtained as above will disclose the presence of iron and alumina, but experience has shown that an equivalent amount of phosphoric acid will be found in the filtrate after the separation of the ammonium magnesium phosphate. The errors are, therefore, mutually compensatory and results obtained agree within the ordinary errors of analysis with those of the molybdenum method.

Our experience having shown us that the above principles could not be applied in the presence of small quantities of phosphoric acid we were led to try the following simple expedient: Whenever we had to deal with a small percentage of phosphoric acid, for instance, anything below ten per cent., we added to the solution, before the precipitation, a sufficient quantity of a solution of a phosphate of known strength to bring the total percentage of phosphoric acid in the mixture up to that of a natural tricalcium phosphate of good quality; *viz.*, from fifteen to thirty per cent. In these circumstances we were able to obtain perfectly accurate results, even in cases where less than one per cent. of phosphoric acid was present. The following analytical data will illustrate the character of the work:

*Solutions Employed.*—No. 1. This is a solution of cottonseed-meal and castor pomace. It is part of a sample sent out last year, by the reporter on phosphoric acid, to the members of the Association of Official Agricultural Chemists.

Nos. 2 to 5 inclusive. These are solutions of natural phosphates containing very small percentages of phosphoric acid, some of them less than one per cent.

Nos. 6 to 10 inclusive. These are preparations made by diluting a standard solution of a superphosphate with water. This superphosphate was a part of a sample sent out by the official reporter for 1894.

Nos. 11 to 17 inclusive. These are natural rock phosphates containing large percentages of phosphoric acid, and the data show the agreement between the direct citrate and the official molybdenum method.

The above solutions for the citrate method were made by treating two grams of the material with fifty cc. of sulphuric acid and

twenty cc. of nitric acid, and boiling until fumes of sulphuric acid began to escape.

## CITRATE METHOD.

Solution No.	Direct. Per cent. $P_2O_5$ .	After adding 25 cc. of known phos- phate solu- tion.		Official molybdenum method. Per cent. $P_2O_5$ .
		Per cent. $P_2O_5$ .	Calculated for original solution. Per cent. $P_2O_5$ .	
1.	1.08	8.93	2.51	2.46
	2.17 <sup>1</sup>	8.97	2.55	2.50
	1.53	15.92	2.61	2.49
	2.30 <sup>1</sup>	15.76	2.45	2.48
2.	0.76	10.91	0.89	1.02
	0.64	11.10	1.08	1.02
3.	3.76	14.10	4.08	4.08
	3.64	14.16	4.14	3.99
4.	0.32	10.78	0.76	0.77
	0.19	10.91	0.89	0.76
5.	0.25	10.82	0.80	0.88
6.	0.76	11.16	1.14	1.15
	0.96	11.16	1.14	1.15
7.	2.17	12.38	2.36	2.30
	2.36	12.31	2.29	2.31
8.	3.25	13.46	3.44	3.44
	3.25	13.46	3.44	3.46
9.	4.40	14.67	4.65	4.62
	4.47	14.48	4.46	4.59
10.	5.68	15.69	5.67	5.74
	5.29	15.63	5.61	5.77
11.	17.23	.....	.....	17.29
12.	37.77	.....	.....	37.77
13.	15.37	.....	.....	15.44
14.	29.16	.....	.....	29.22
15.	29.49	.....	.....	29.47
16.	31.64	.....	.....	31.64
17.	32.22	.....	.....	32.15

*Explanatory Notes.*—With solution No. 1 four determinations were made. In the first and third instances the mixture was allowed to stand twenty-four hours before filtering, while in the third and fourth instances it was allowed to remain for three days. The results clearly show the progressive separation of the crystalline precipitate, almost the full quantity being secured after the lapse of three days. In the first and second instances there was added enough of a solution of rock phosphate to bring the total phosphoric acid up to about nine per cent., while in the third and fourth determinations a solution of a richer rock was added, bringing the total phosphoric acid in the mixture up to about sixteen per cent. There was little difference noted in the

<sup>1</sup> Stood 72 hours.



results. Beginning with solution No. 2, the increase in the content of phosphoric acid was secured by adding measured quantities of a solution of ammonium phosphate of known strength. The results show that a chemically pure phosphate can be used with equal safety in place of solutions of rock phosphate. By a study of the results obtained with solution 10, it is seen that when the content of phosphoric acid reaches about six per cent. the direct method with magnesium citrate gives approximately correct results. It is to be recommended, however, in all cases where the sample contains less than ten per cent., that fortification with a solution of a phosphate of known strength be practiced.

Solutions 11 to 17 inclusive were made from samples of rock phosphate quite rich in phosphoric acid and, therefore, required no fortification. It is seen in all cases that the data obtained by the direct citrate method are almost identical with those secured by the official molybdenum process.

*Conclusions.*—(1) In all cases of samples of tricalcium phosphate, or acid phosphates made therefrom, containing the usual accompanying substances, the phosphoric acid may be correctly estimated by direct precipitation with magnesium citrate.

(2) In all cases of the analysis of natural rock phosphates containing less than five per cent. of phosphoric acid it is necessary to fortify the solution before precipitation by adding a measured quantity of a solution of phosphoric acid of known strength.

(3) The fortifying solutions employed may be made either from natural tricalcium phosphates or from chemically pure phosphate salts.

(4) The direct precipitation of the phosphoric acid in the presence of ammonium citrate by ammoniacal magnesia mixture is a quicker and less expensive process than the official molybdenum method and leads to results equally accurate.

(5) We have not applied the direct citrate method to the natural iron and aluminum phosphates, and therefore can make no statement in regard to its accuracy in the treatment of such samples.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF OBERLIN  
COLLEGE.]

## AN ARRANGEMENT FOR WASHING PRECIPITATES WITH BOILING WATER.

BY FRANK F. JEWETT.

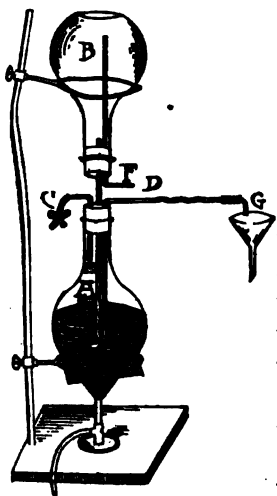
Received February 7, 1895.

Using the ordinary wash-bottle for boiling water, the mouth-piece is not infrequently so much heated by escaping steam that the lips, when applied to it in the usual manner, are either uncomfortably overheated or positively burned. To avoid this result the apparatus, herein described, was devised, and has worked with perfect satisfaction.

Two flasks are arranged as shown in the figure. To the lower one, A, is fitted a rubber stopper through which pass three glass tubes. A short one, bent at right angles, just enters the flask, and to its outer extremity is attached a short rubber tube provided with a spring clip C.

A long tube reaches to the bottom of the flask and extends six or eight inches at right angles from a point just above the stopper. To its outer end is attached a rubber tube a few inches long, into which is fitted a glass jet, G, bent at right angles and wound about with a strip of felt or other non-conducting material. A third tube, E, extends from the bottom of the lower flask just through the stopper of the upper flask B, which is also provided with the tube F reaching to the top of the flask.

To use the apparatus, the water is heated to gentle boiling, the steam passing out through the open clip C. When a precipitate is to be washed, the clip is closed and the pressure of the steam at once drives the water out through the tube D. By clamping the non-



conducting cover of the jet G with the thumb and finger, the stream of boiling water may be directed to any place desired. Any excess of pressure simply drives the water slowly through the tube E into the upper flask, from which the air escapes through F.

When a sufficient quantity of water has been used, the clip is opened, the jet G raised, and the water immediately returns to the lower flask.

OBERLIN, OHIO.

## INTERPRETATION OF SOME RESULTS IN THE ANALYSIS OF EXTRACTS OF FUSTIC.

BY CHARLES S. BOYER.

Received April 13, 1895.

SOME time since, the writer made several analyses of samples of extract of fustic, the method of whose manufacture was at the time unknown. Since there are no recorded analyses of extracts of fustic, so far as I can find, it was thought that a statement of the results and conclusions might be of interest to those engaged in this line of work.

The method of analysis employed is briefly as follows: Five to six grams of the extract were carefully dried in a water-bath until no further loss occurred, the loss being regarded as water. Two to four grams of this dry powder was now put into a Soxhlet extractor and thoroughly and repeatedly exhausted with *absolute* alcohol, the alcoholic extract distilled, and the residue dried and weighed. The residue was in every case treated with boiling water and tested for *morin* and *maclurin* (*morin-lannin*), the former by adding to one portion a few drops of aluminum sulphate and the latter by adding to another portion some ferric chloride, but in each case with negative results. The residue from the alcoholic extract was ignited in a platinum crucible and the ash subtracted from the matter soluble in absolute alcohol. For the ash percentage, five grams of the powder was carefully ignited in a capacious platinum crucible and the resulting ash weighed.

The results of the analysis of three extracts of fustic found upon the market, together with those of two extracts whose methods of manufacture were known, are put into a table below.

The results are also calculated upon a dry basis so that they may be compared the better.

	I.			II.			III.			IV.			V.		
	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.
Water.....	67.09	....	50.42	....	36.48	....	49.62	....	6.18	....					
Organic matter soluble in absolute alcohol.....	31.34	95.23	38.57	77.79	52.85	83.20	47.41	94.11	75.55	80.53					
Ash .....	0.52	1.58	5.54	11.18	1.24	1.95	1.05	2.08	7.62	8.12					
Organic matter insoluble in alcohol.....	1.05	3.19	5.47	11.03	9.43	14.85	1.92	3.81	10.65	11.35					
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00					

Sample IV was made in an open extractor, the water used in the extraction being brought to a boil before it was run on the wood and the length of time that each "water" remained in contact with the wood being fifteen minutes. Eight "waters" were taken off. Sample V was extracted under five pounds pressure, using seven waters and the weak liquor being evaporated to dryness.

It will be seen that Sample I is very similar to IV, while the analysis of II and V are very much alike, especially in that both have a high percentage of ash and approximately the same amounts of organic matter insoluble in alcohol.

It is quite true that different brands of fustic, and even different cargoes of the same brand, contain varying percentages of inorganic matter, or ash. This might lead one to erroneous conclusions were one to depend entirely upon the ash percentages. However, the chief mineral constituents of fustic are lime and magnesia, and as a result of a large number of analyses the writer finds that these two ingredients form another guide in determining the method of extraction. The more pressure used in the extraction, the higher, within certain limits, the ash percentage, and also the larger the amount of lime and magnesia contained in the ash. In the extracts under investigation the percentages of lime and magnesia together were in I, 41.16 per cent.; IV, 46.83 per cent.; II, 68.12 per cent.; and V, 62.15 per cent. of the total ash.

Another ingredient which might prove misleading is extract of quercitron bark. In order to ascertain whether any of these extracts contained this adulterant, a series of dye-tests were

made depending upon the different affinities of the coloring principles of bark and fustic for alum and tin mordants, but in none of them could any admixture with quercitron bark extract be detected.

The conclusions drawn from these analyses and comparisons were that I was made entirely by the "open-extraction" method; II was made by the "closed-extraction" method, using five to eight pounds pressure; and that III was extracted in open vessels, but that the changes of "waters" was done under pressure. The reason for the latter conclusion was that, while the ash percentage was low, the "extractive matter," or organic matter insoluble in alcohol was very high and the only way that this could happen would be by opening up the fiber of the wood, as is the case in open boiling and then applying pressure, which carried this "extractive matter" into the extracting liquor. These conclusions were subsequently borne out by experiments.

CAMDEN, N. J., April 6, 1895.

## THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.

BY FANNY R. M. HITCHCOCK.

[Continued from page 494.]

*b.* Five cc. of the cerium sulphate solution were diluted to sixty cc., and brought to boiling, when alcohol was added, five cc. at a time, until sixty-five cc. had gone in, but the solution still remained clear. To this hot solution the cerium sulphate solution was added in the same way as the alcohol had been. The first addition of five cc. caused a precipitate to form, which redissolved at once. The second addition of five cc. caused a precipitate which dissolved again very slowly, and with the third addition the cerium sulphate came down in fine needles.

It was evident that the amount of alcohol which had been used in experiments 8, 9 and 10, with the sodium molybdate, had not been sufficiently great to cause by itself the precipitation of the cerium sulphate. The experiments were, therefore, repeated, the conditions being slightly varied.

*Experiment 11.* Ten cc. sodium molybdate solution were diluted to 100 cc., and fifteen cc. of the cerium sulphate solution added. To this, in the cold, fifty cc. of ninety-five per cent. alcohol were added very gradually, and with constant stirring. The

whole was allowed to stand for half an hour, when the precipitate was filtered off, washed, first with fifty per cent. alcohol, then with thirty per cent., and finally with pure water, ignited, and weighed. The results obtained were the best of all the series.

Wt. obtained.	Calculated.	Difference.
0.1620 gram.	0.1629	—0.0009

The ignited precipitate dissolved in hydrochloric acid gave no trace of sulphuric acid when tested with barium chloride.

*Experiment 12.*—This was a duplicate of No. 11, except that the final washing was done with twenty per cent. alcohol instead of pure water. The washing was continued until there was no reaction with barium chloride for sulphuric acid.

Wt. obtained.	Calculated.	Difference.
0.1799 gram.	0.1629	+0.0170

The precipitate was tested as before, and proved to contain cerium sulphate.

*Experiment 13.*—Ten cc. of sodium molybdate solution were diluted to 185 cc. and fifty cc. of ninety-five per cent. alcohol added, followed by fifteen cc. of cerium sulphate solution. After standing an hour the precipitate was filtered off, and washed in the same manner as in No. 12.

Wt. obtained.	Calculated.	Difference.
0.1644 gram.	0.1629	0.0015

From the precipitate barium sulphate equivalent to 0.00146 gram of cerium sulphate was obtained, and the filtrate gave 0.0007 gram of molybdenum trisulphide.

*Experiment 14.*—This was a duplicate of No. 13.

Wt. obtained.	Calculated.	Difference.
0.1708 gram.	0.1629	0.0079

The precipitate yielded the equivalent of 0.0090 gram of cerium sulphate with barium chloride.

With hydrogen sulphide a precipitate of molybdenum trisulphide was given by all the filtrates from the experiments described above, the amount varying in wide limits. While alcohol diminished the solubility of the cerium molybdate formed, the advantage gained was more than counterbalanced by the tendency of the molybdate to carry down with it cerium sulphate in the presence of alcohol.

## SODIUM TUNGSTATE AND CERIUM SULPHATE.

The solution of sodium tungstate used contained 27.07 grams in one liter. But few experiments were made, the results obtained being similar to those with sodium molybdate. Precipitation in a water solution alone was very incomplete, the precipitate persistently running through the filter, so that no definite results could be obtained in this way. When alcohol was used better results were obtained, the filtrate coming through clear.

*Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling when twenty-five cc. cerium sulphate solution were added. A dense, flocculent yellow-white precipitate came down at once, subsiding rapidly; it was filtered and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3266 gram.	0.3144	0.0122

*Experiment 2.*—Ten cc. of sodium tungstate solution were diluted with distilled water to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added, followed by twenty-five cc. of cerium sulphate solution in the cold. A bluish white precipitate formed, which on standing acquired a yellow tint. This was filtered cold and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3125 gram.	0.3144	—0.0019

*Experiment 3.*—Ten cc. of sodium tungstate solution were diluted to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling and twenty-five cc. cerium sulphate added. The precipitate was washed with hot twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3322 gram.	0.3144	0.0178

The precipitate from all three solutions contained cerium sulphate, and the filtrates all showed traces of tungsten.

The next salts taken up were the two very rare ones, neodymium chloride and praseodymium chloride. For the material used I am indebted to the courtesy of Professor Waldron Shapleigh, of the Welsbach Light Company, Gloucester, N. J. The material given me consisted of the oxides prepared from the



oxalates by ignition. These oxides are considered by v. Welsbach<sup>1</sup> to be the peroxides, and the formulas  $\text{Nd}_2\text{O}_5$  and  $\text{Pr}_2\text{O}_5$  have been assigned to them.

$\text{Nd}_2\text{O}_5$  is a light brown powder, while  $\text{Pr}_2\text{O}_5$  is dark brown, almost black. Both dissolve readily in hydrochloric acid with evolution of chlorine, and form sesquichlorides. Neodymium chloride,  $\text{Nd}_2\text{Cl}_6$ , forms a rose colored solution while the corresponding praseodymium salt is pale green in color. The solutions used were prepared by evaporating the chlorides prepared from the oxides to dryness, taking up with water and again evaporating until all the hydrochloric acid was expelled. The residue was dissolved in water and filtered off from a little insoluble material which was probably a basic salt. About half a gram of the oxide was taken, and from it 100 cc. of the chloride solution was prepared.

The tungstates obtained from these salts by precipitation with sodium tungstate were gelatinous, and very difficult to filter and wash, showing a strong tendency to pass through the pores of the filter-paper.

For this reason a double filter was always used, and even with this precaution it was necessary to use as little pressure as possible with the filter-pump, and yet secure filtration. Even with the filter-pump the washing was very slow, and generally consumed a day at least, sometimes longer, although the quantities of material used were very small. The best results were obtained by washing first by decantation, and then on the filter.

The molybdates are gelatinous when first precipitated, but on heating they gradually become granular, and are then easily filtered and washed.

The neodymium tungstate has a very pale rose tint before ignition, which changes to a lavender color after ignition. The praseodymium tungstate has a decided greenish yellow tint both before and after ignition. The colors of the molybdates were similar to those of the tungstates, but deeper in tint.

The tendency of the precipitates to adhere to the sides of the beaker was a serious source of error at first; particularly after boiling, when it seemed impossible to remove them entirely. If not heated above  $70^\circ \text{C}$ . a piece of moist filter will remove the

<sup>1</sup> *Wien. Monatsheft*, 6, 477, 1885.

adherent precipitate better than anything; in most cases it removes it perfectly, while a rubber is useless.

The ignitions were all made with free access of air, and were continued for at least two hours. Apparently no reduction of the molybdic acid takes place, as a second ignition after moistening with ammonium nitrate or with nitric acid, causes no change in the weight.

The solubilities were determined by the Victor Meyer method.<sup>1</sup> It will be noticed that with the praseodymium salts the solubility increases with a rise in temperature, the increase being more marked with the tungstate than with the molybdate.

With neodymium tungstate the solubility decreases as the temperature rises, while with the molybdate it increases under the same conditions. Slight though the solubility is, it is sufficiently great to cause decided error in the results when such small quantities are taken as were used in the experiments here recorded.

It was found very difficult at first, when analyzing the salts, to obtain a constant weight for the oxides, the results being all higher than theory required. The method finally adopted proved very satisfactory. The precipitated oxalate was strongly ignited together with the filter-paper, in a covered platinum crucible, for half an hour, cooled, and moistened with saturated solution of oxalic acid, then ignited again in the covered crucible.

The excess of weight in the earlier analyses being greater than was called for by oxidation to the peroxides,  $\text{Nd}_2\text{O}_5$  and  $\text{Pr}_2\text{O}_5$ , the following experiments were made to determine how much oxygen would be taken up by the oxides after they had been reduced to the sesquioxides. In the analyses of neodymium molybdate, the theoretical amount required for the quantity taken was 0.0865 gram; the amount obtained was 0.0863 gram. This was heated in a platinum crucible with a Bunsen burner, the flame being applied at the back of the crucible, while the oxide was drawn forward to prevent any action of reducing gases, as far as possible. The cover of the crucible was bent and placed so as to cause a current of air to pass over the oxide.

<sup>1</sup> *Ber. d. chem. Ges.*, 8, 998, 1875.



From time to time the crucible was cooled and weighed. The following table shows the gain in weight observed and the length of time for which the heat had been applied. It is assumed that the weight first taken represents the sesquioxide, and the atomic mass is taken as 140.5.

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0863 gram.	0.0000	$\text{Nd}_2\text{O}_3$ .
4 "	0.0888 "	0.0025	$\text{Nd}_2\text{O}_7$ .
5 "	0.0892 "	0.0029	
7½ "	0.0906 "	0.0043	$\text{Nd}_2\text{O}_4$ ?
10½ "	0.0937 "	0.0074	
16 "	0.0958 "	0.0095	
22 "	0.0997 "	0.0134	$\text{Nd}_2\text{O}_6$ ?
27½ "	0.1035 "	0.0172	$\text{Nd}_2\text{O}_7$ ?
30½ "	0.1036 "	0.0173	

The oxide on first heating changed to light brown, the color of the superoxide prepared by the Welsbach Company; as the heat was continued it grew lighter in color, until, when it had attained its maximum weight, it was almost pure white.

If the flame be placed directly under the oxide, it loses weight and gradually passes into the brown "superoxide,"  $\text{Nd}_2\text{O}_7$ .

A similar experiment with praseodymium sesquioxide,  $\text{Pr}_2\text{O}_3$ , gave the following results :

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0668 gram.	0.0000	$\text{Pr}_2\text{O}_3$ .
4 "	0.0706 "	0.0038	$\text{Pr}_2\text{O}_4$ ?
6 "	0.0722 "	0.0054	
8 "	0.0730 "	0.0062	$\text{Pr}_2\text{O}_5$ ?
11 "	0.0745 "	0.0077	
13 "	0.0749 "	0.0081	

The atomic mass of praseodymium is taken at 143.5. The color of the oxide changed in the same way as that of neodymium, passing rapidly into the black peroxide  $\text{Pr}_2\text{O}_7$  of Welsbach, then slowly changing to a reddish brown, and gradually becoming quite light in color. Whether it would be possible to increase the weight still more by heating small quantities for a long period of time, can only be determined by experiment; but the indications point to the existence of praseodymium trioxide  $\text{Pr}_2\text{O}_5$ , as the increase in weight obtained is greater than that required for  $\text{Pr}_2\text{O}_6$ .

It would appear that the oxide  $\text{Nd}_2\text{O}_3$  can be formed, improbable as it may seem, and that it is comparatively stable.

If it is really  $\text{Nd}_2\text{O}_3$ , neodymium is properly classed with manganese in the seventh group. It would be interesting to know if by reduction the monoxide  $\text{NdO}$  could also be formed.

#### SODIUM TUNGSTATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium tungstate contained five grams in one liter.

*Experiment 1.*—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol were added, followed by five cc. of praseodymium chloride solution in the cold. A precipitate formed at once, and the whole was boiled for an hour. It was then filtered, washed with hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

Wt. obtained.	Calculated.	Difference.
0.0579 gram.	0.0586	—0.0007

*Experiment 2.*—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of alcohol added. The whole was brought to boiling, and five cc. of the praseodymium chloride solution added, after which the boiling was continued for an hour. The precipitate was then filtered off, and washed with cold water containing twenty per cent. of alcohol. The filtrate showed a slight opalescence, which was not removed by refiltering.

Wt. obtained.	Calculated.	Difference.
0.0540 gram.	0.0586	—0.0046

*Experiment 3.*—Twenty cc. of the sodium tungstate solution were diluted with seventy-five cc. of distilled water, and five cc. of the praseodymium chloride added. The whole was then boiled for an hour, allowed to cool, and filtered cold, the washing being done with cold water.

Wt. obtained.	Calculated.	Difference.
0.1091 gram.	0.1172	—0.0081

*Experiment 4.*—Twenty cc. of sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added. The whole was allowed to

stand for twelve hours, then brought to boiling, filtered hot, and washed with boiling water.

Wt. obtained.	Calculated.	Difference.
0.1136 gram.	0.1172	—0.0036

The filtrate was boiled for an hour with fifty cc. of ninety-five per cent. alcohol, but no additional precipitate was obtained.

*Experiments 5 and 6.*—Twenty cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added, followed by fifty cc. of ninety-five per cent. alcohol. The whole was then boiled, filtered while hot, and washed with hot water containing thirty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 5.</i>	0.1200 gram.	0.1172	0.0028
" 6.	0.1230 "	0.1172	0.0058

*Experiments 7, 8, and 9.*—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, and six cc. of the praseodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was heated to 60° C. for half an hour, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 7.</i>	0.1733 gram.	0.1758	—0.0025
" 8.	0.1730 "	0.1758	—0.0028
" 9.	0.1724 "	0.1758	—0.0034

The precipitates after ignition showed traces of the blackish-brown praseodymium peroxide  $\text{Pr}_2\text{O}_5$ . The filtrate was tested with hydrogen sulphide, but gave no reaction for tungsten.

*Experiments 10, 11, 12, 13, and 14.*—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, six cc. of the praseodymium chloride solution, and twenty-five cc. of alcohol added, and the whole heated for two hours at a temperature of 60° C. The precipitate was filtered off while the solution was hot, and was washed with 150 cc. hot water, containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 10.</i>	0.1715 gram.	0.1758	—0.0043
" 11.	0.1712 "	0.1758	—0.0046
" 12.	0.1713 "	0.1758	—0.0045
" 13.	0.1712 "	0.1758	—0.0046
" 14.	0.1713 "	0.1758	—0.0045

The ignited precipitates appeared to be homogeneous, with traces of  $\text{Pr}_2\text{O}_3$  showing.

The filtrates were all tested for tungsten with hydrogen sulphide, but no tungsten trisulphide was obtained. This test is not of much value, however, when alcohol is present, as that will prevent the precipitation of tungsten as sulphide to a great extent, so that small quantities will escape detection, unless the alcohol is removed by evaporation before the hydrogen sulphide is used. The precipitation of molybdenum does not seem to be hindered under the same conditions, the hydrogen sulphide bringing down minute traces in a solution containing thirty-three per cent. of alcohol.

As the error is constant, and the condition of precipitation the same for all the numbers of this series of experiments, it is probably due to the solubility of praseodymium tungstate in water containing alcohol.

#### ANALYSIS OF PRASEODYMIUM TUNGSTATE.

One-tenth of a gram of the salt was fused with three grams of equal parts of sodium carbonate and sulphur. The fused mass was taken up with water, the gray-green insoluble residue filtered off, and washed with cold water; the filtrate was acidified with hydrochloric acid, the precipitated tungsten trisulphide filtered off on a tared filter, and dried in the air-bath at  $100^\circ\text{C}$  until a constant weight was obtained.

When allowance is made for the molybdic acid present in sodium tungstate the amount of sulphide obtained must be lower than that called for by theory for pure praseodymium tungstate. The praseodymium oxide should be slightly higher in amount.

To estimate the oxide the insoluble residue from the fusion was dissolved in hydrochloric acid, precipitated with oxalic acid and ammonium hydroxide, and ignited in a covered crucible as already described.

	Wt. obtained.	Calculated.	Theoretical.
$\text{Pr}_2\text{O}_3$	0.0334 gram.	0.0331	0.0325
$\text{WS}_3$	0.0806 "	0.0808	0.0814

These results leave no doubt but that the constitution of the salt is correctly represented by the formula  $\text{Pr}_2(\text{WO}_4)_3$ .

To determine the solubility of the salt, praseodymium chloride

was precipitated by sodium tungstate in aqueous solution; the precipitate with the solution was heated to 60°C. for two hours before filtering, and was washed with hot water until silver nitrate showed no trace of chlorine. The precipitate was dried in the air for a week, and then finely powdered. Portions of the salt were mixed with distilled water at different temperatures, about eighty cc. of water being taken for each portion, and then allowed to stand for two hours, the temperature being kept constant and the liquid frequently stirred. At the end of two hours they were filtered into weighed porcelain crucibles, evaporated to dryness, ignited, and weighed.

The results obtained are given below:

Temperature.	Wt. of solution.	$\text{Pr}_2(\text{WO}_4)_2$ .	Solubility.
20° C.	39.3817 grams.	0.0000	0:00000
20° C.	44.6541 "	0.0000	0:00000
75° C.	44.2312 "	0.0019	1:23300
75° C.	40.1484 "	0.0018	1:22300

#### SODIUM MOLYBDATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

*Experiments 1-6.*—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water, then twelve cc. praseodymium chloride solution were added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 65° C. The precipitate was then filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.2093 gram.	0.2101	—0.0008
" 2.	0.2094 "	0.2101	—0.0007
" 3.	0.2096 "	0.2101	—0.0005
" 4.	0.2084 "	0.2101	—0.0017
" 5.	0.2084 "	0.2101	—0.0017
" 6.	0.2080 "	0.2101	—0.0021

The precipitates numbered 1, 2, and 3, all showed traces of praseodymium oxide  $\text{Pr}_2\text{O}_3$ ; the others seemed to be homogeneous.

The filtrates were all tested for molybdenum, with zinc, hydrochloric acid and potassium thiocyanate, but none was found. Alcohol does not interfere with the delicacy of this test.

The ignited salt was analyzed, the molybdic acid being determined by the Pechard method, while the praseodymium oxide was determined in the residue, after the molybdic acid was expelled, by the same method as had been pursued with the tungstate.

	Wt. obtained.	Calculated.
WO <sub>3</sub>	0.1135 gram.	0.1127
Pr <sub>2</sub> O <sub>3</sub>	0.0874 "	0.0873

The amount taken for analysis was two-tenths of a gram, and the results show the correct formula to be Pr<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, corresponding to that found for the tungstate.

The solubility of praseodymium molybdate was determined with the following results:

Temperature.	Wt. of solution.	Pr <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> .	Solubility.
23° C.	71.4000 grams.	0.0011	1:65820
75° C.	69.8000 "	0.0010	1:69800

#### PRECIPITATION OF TUNGSTIC ACID WITH NEODYMIUM CHLORIDE.

The solution of sodium tungstate used contained five grams in one liter.

*Experiments 1 and 2.*—Twenty cc. of the sodium tungstate were diluted to 100 cc. with distilled water and five cc. of the neodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was brought to boiling, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

The filtrates were opalescent, and repeated filtrations failed to render them clear. The precipitates, after ignition, appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1117 gram	0.1167	—0.0050
" 2.	0.1126 "	0.1167	—0.0041

*Experiments 3 and 4.*—Ten cc. of the sodium tungstate solution diluted to fifty cc. with distilled water, and three and one-half cc. of neodymium chloride solution added were heated to boiling, filtered while hot, and the precipitate washed with hot water.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 3.</i>	0.0595 gram.	0.0583	0.0012
" 4.	0.0573 "	0.0583	—0.0010

*Experiments 5-16.*—These experiments were duplicates of 3 and 4, excepting that the solutions were heated to 80° C. instead of to boiling. No alcohol was added, and the precipitates were washed with hot water. The precipitates showed traces of the brown peroxide,  $\text{Nd}_2\text{O}_3$ .

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 5.</i>	0.0575 gram.	0.0583	—0.0008
" 6.	0.0575 "	0.0583	—0.0008
" 7.	0.0593 "	0.0583	+0.0001
" 8.	0.0600 "	0.0583	0.0017
" 9.	0.0585 "	0.0583	0.0002
" 10.	0.0586 "	0.0583	0.0003
" 11.	0.0590 "	0.0583	0.0007
" 12.	0.0585 "	0.0583	0.0002
" 13.	0.0585 "	0.0583	0.0002
" 14.	0.0581 "	0.0583	—0.0002
" 15.	0.0584 "	0.0583	0.0001
" 16.	0.0597 "	0.0583	0.0014

*Experiments 17 and 18.*—Thirty cc. of the sodium tungstate solution were diluted to seventy cc. with distilled water and six cc. of the neodymium chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated to 70° C., filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 17.</i>	0.1724 gram.	0.1749	—0.0025
" 18.	0.1745 "	0.1749	—0.0004

No. 18 showed slight traces of the peroxide  $\text{Nd}_2\text{O}_3$ .

*Experiments 19-21.*—These were prepared like the preceding solutions Nos. 17 and 18, but were heated to 60° C. instead of 70°.

The filtrates showed no trace of molybdenum when tested with zinc, hydrochloric acid, and potassium thiocyanate.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 19.</i>	0.1731 gram.	0.1749	—0.0018
" 20.	0.1727 "	0.1749	—0.0022
" 21.	0.1728 "	0.1749	—0.0021

A comparison of these results shows that the precipitation of tungstic acid by neodymium chloride is practically quantitative. Analyses of the salt made in the same manner as for praseodymium tungstate agreed closely with the theoretical requirements as regarded the neodymium oxide. The tungstic acid was inva-



riably too low, and the different results were too discordant; the tungstic acid, therefore, was determined by difference; the weight of neodymium oxide found was 0.0651 gram, the amount required by theory being 0.0652 gram. From this was deduced the formula  $\text{Nd}_2(\text{WO}_4)_3$  for the salt, which corresponds to the praseodymium tungstate.

The solubilities, determined as for the praseodymium salts, and under similar conditions were as follows:

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{WO}_4)_3$ .	Solubility.
22° C.	42.1032 grams.	0.0008	1:52630
65° C.	41.7117 "	0.0007	1:59580
98° C.	39.6286 "	0.0006	1:66040

#### SODIUM MOLYBDATE AND NEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 5.1080 grams in one liter.

*Experiments 1-5.*—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water; seven cc. of the neodymium chloride solution were added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was then heated to 65° C. for two hours, filtered hot, and the precipitate washed with 150 cc. of hot water containing twenty-five per cent. of alcohol.

The ignited precipitates showed no trace of the brown oxide  $\text{Nd}_2\text{O}_3$ , and the filtrates, when tested, gave no reaction for molybdenum.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1260 gram.	0.1256	0.0004
" 2.	0.1259 "	0.1256	0.0003
" 3.	0.1260 "	0.1256	0.0004
" 4.	0.1259 "	0.1256	0.0003
" 5.	0.1258 "	0.1256	0.0002

An analysis of two-tenths of a gram of the salt made in the same way as the analysis of praseodymium molybdate gave the following results:

	Wt. obtained.	Calculated.	Difference.
$\text{Nd}_2\text{O}_3$	0.0863 gram.	0.0865	—0.0002
$\text{MoO}_3$	0.1134 "	0.1135	—0.0001

From these results the formula  $\text{Nd}_2(\text{MoO}_4)_3$  is deduced for neodymium molybdate.



The solubility determinations gave the following results :

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{MoO}_4)_3$ .	Solubility.
28° C.	69.9311 grams.	0.0013	1:53790
75° C.	71.4279 "	0.0022	1:32466

A comparison of the results obtained shows that the precipitation of both tungstic and molybdic acids by neodymium salts is quantitative.

#### SODIUM TUNGSTATE AND LANTHANUM CHLORIDE.

The solution of sodium tungstate contained five grams in a liter.

*Experiments 1 and 2.*—Twenty cc. of sodium tungstate solution were diluted to seventy cc. with distilled water, and seven cc. of lanthanum chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 60° C., after which the precipitate was filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol. The filtrate was clear and gave no reaction for tungsten with hydrogen sulphide. The ignited precipitates appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1143 gram.	0.1160	—0.0017
" 2.	0.1143 "	0.1160	—0.0017

The tungstate before ignition was of a delicate blue, almost white, and after ignition the color deepened slightly. The color of the molybdate was almost the same as that of the tungstate.

#### ANALYSIS OF LANTHANUM TUNGSTATE.

The first analysis was made by fusing with sodium carbonate and sulphur, then taking up in water, and filtering off the sodium sulphotungstate formed, from the insoluble lanthanum oxide; then decomposing the filtrate with hydrochloric acid and estimating the tungsten from the tungsten trisulphide found.

The results obtained were very satisfactory so far as the lanthanum oxide was concerned, but no good results were obtained for the tungstic acid.

The amount of the salt taken for analysis was one-tenth of a gram.

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$	0.0326 gram.	0.0321
$\text{WS}_3$	0.0606 "	0.0822

The same difficulty was encountered here that was met with in the analysis of neodymium tungstate, and the cause was not apparent. A second analysis by a different method was made the same amount of material being taken. The lanthanum tungstate was decomposed with aqua regia, evaporated to dryness with hydrochloric acid three times, and the separated tungsten trioxide filtered off and dissolved in ammonium hydroxide; the filtrate was rendered ammoniacal, the solution of the tungstic acid added to it, and hydrogen sulphide passed through it until the liquid was deep yellow in color. The liquid was acidified with hydrochloric acid, and before neutralization was complete the color changed to a bright green, becoming red when completely acidified. On rendering it ammoniacal again, the green color reappeared.

Hydrogen sulphide was passed through the solution again for an hour, hydrochloric acid added, and the solution warmed; it gradually became colorless, and a light brown precipitate of tungsten trisulphide settled down.

This was treated in the usual manner and dried at 100° to constant weight.

	Wt. obtained.	Calculated.
WS <sub>3</sub>	0.0640 gram.	0.0822

The filtrate was boiled until all the hydrogen sulphide was expelled, a few drops of nitric acid added, and then ammonium hydroxide; the precipitate of lanthanum hydroxide was evidently not pure, being yellow in color instead of white; it was filtered off, ignited, dissolved in aqua regia, evaporated to dryness, taken up with a little hydrochloric acid, followed by ammonia, and the treatment with hydrogen sulphide repeated. The yellow ammoniacal solution passed through the same color changes as before, when acidified. On heating, a dark red-brown precipitate formed which was filtered off, and washed with dilute hydrochloric acid, and then with alcohol. A great part of the precipitate dissolved in the alcohol to a dark red solution, the precipitate left on the filter-paper turning brown. This precipitate was ignited in a weighed porcelain crucible and evaporated with concentrated nitric acid until a constant weight was obtained. It had the appearance of tungstic acid.

Wt. obtained = 0.0073 gram.

The alcoholic filtrate was evaporated to dryness in a weighed porcelain crucible, and treated repeatedly with fuming nitric acid to oxidize any sulphur that might be present to sulphuric acid, which was removed by repeated evaporation with ammonium hydroxide. The substance remaining in the porcelain crucible had the appearance of molybdic acid. It was pale yellow in color, was readily soluble in ammonium hydroxide, and also dissolved in aqua regia to a bright yellow solution, separating out as a bright yellow powder on concentrating the solution. The yellow powder, when ignited, turned brown, but regained its color on cooling, finally, however, becoming lemon-yellow. When moistened with hydrochloric acid and heated, no blue color appeared. A faint orange-red solution was obtained by treatment with zinc, hydrochloric acid, and potassium thiocyanate. Heated on platinum foil with concentrated sulphuric acid no blue color was produced. The phosphorus bead was colorless, even after treating with tin on charcoal.

The weight obtained was 0.0076 gram. The second analysis gives the following results:

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$ .	0.0326	0.0321
$\text{WO}_3$ .	0.0613	0.0679
	0.0076	

This corresponds to the formula  $\text{La}_2(\text{WO}_4)_3$ , for lanthanum tungstate. The same salt was prepared by W. French Smith<sup>1</sup> by the precipitation of sodium tungstate with lanthanum salts.

The solubility of lanthanum tungstate in water was determined by the Victor Meyer method, the salt being prepared in the same way as the praseodymium tungstate.

Temperature.	Wt. of solution.	$\text{La}_2(\text{WO}_4)_3$ .	Solubility.
27° C.	60.5580 grams.	0.0007	1:86510
65° C.	42.4678 "	0.0010	1:42467

#### SODIUM MOLYBDATE AND LANTHANUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

*Experiments 1-3.*—Twenty cc. sodium molybdate solution were diluted to seventy cc. with distilled water, seven cc. of lantha-

<sup>1</sup> "Ueber Didymium and Lanthanum." Inaugural Dissertation by W. French Smith. Göttingen, 1876.

num chloride solution added, followed by twenty-five cc. of ninety-five per cent. alcohol.

The precipitate, at first gelatinous, gradually became granular, and was filtered off, washed with 150 cc. hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.2063 gram.	0.2083	—0.0020
" 2.	0.2061 "	0.2083	—0.0022
" 3.	0.2063 "	0.2083	—0.0020

The filtrates were clear and gave no reaction for molybdenum when treated with potassium thiocyanate in the presence of zinc and hydrochloric acid.

The solubility of the salt obtained was determined under the following conditions:

Temperature.	Wt. of solution.	$\text{La}_2(\text{MoO}_4)_3$ .	Solubility.
25° C.	72.5500 grams.	0.0013	1:55800
85° C.	69.3474 "	0.0023	1:30150

#### ANALYSIS OF LANTHANUM MOLYBDATE.

The analysis was made in the same manner as with the other molybdates, the salt being decomposed in a current of dry hydrogen chloride gas. The molybdic acid was driven off very readily at first, but toward the close of the operation the full heat of the Bunsen burner was required. Two-tenths of a gram of the salt were taken for analysis, and results were as follows:

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$	0.0853	0.0856
$\text{MoO}_3$	0.1145	0.1144

From these results the formula  $\text{La}_2(\text{MoO}_4)_3$  may be calculated for lanthanum molybdate.

Tests were now made with thorium chloride, potassium zirconium fluoride, and zirconium fluoride.

With thorium chloride no definite results could be obtained from either sodium molybdate or sodium tungstate; precipitates were formed with both salts even in quite dilute solutions, but they were slight in quantity, and ran through the filter in spite of every attempt to prevent it, whether filtered hot or cold. Neither alcohol nor ammonium salts made any difference in the behavior.

With the potassium zirconium fluoride no precipitate was obtained with either the sodium tungstate or molybdate.

With zirconium fluoride no results were obtained, the solutions remaining clear after standing several days.

Beyond these qualitative tests no work was done with the thorium or zirconium salts in connection with tungsten and molybdenum.

#### SUMMARY.

1. The tungstates and molybdates are precipitated quantitatively by nearly all the rare earths.
2. A separation of tungstic and molybdic acids is not possible through their combinations with the rare earths.
3. The non-precipitation of molybdic acid by uranyl solutions when tungstates are absent, and the almost complete precipitation of both when tungstic acid is also present is further evidence of the fact that we can scarcely hope to effect this separation by the method of precipitation.
4. The molybdates and tungstates of neodymium and praseodymium are new, and their constitution is correctly represented by the formula  $Nd_2(MoO_4)_3$ ,  $Nd_2(WO_4)_3$ , and  $Pr_2(MoO_4)_3$ ,  $Pr_2(WO_4)_3$ .
5. The solubility determinations indicate that tungstates and molybdates of the rare earths must be classed among the more difficultly soluble compounds.
6. Further research is required upon the methods to be followed in the separation of tungstic and molybdic acids from the oxides of the rare earths.

### A NEW TABLE FOR THE QUALITATIVE SEPARATION OF THE METALS OF THE IRON GROUP.

By C. L. HARR.

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IN the qualitative separation of metals of the iron group much trouble has been experienced with the methods in general use for the separation of cobalt and nickel.

The methods commonly used for the separation of iron, aluminum, and chromium are also unsatisfactory.

The following compilation and application of methods recently worked up greatly simplifies and shortens the process for the qualitative separation of the metals of this group.



In the separation of chromium from iron and aluminum advantage is taken of the well-known action of hydrogen peroxide on chromium compounds in presence of an alkali, the insoluble chromium compound being oxidized to soluble chromic acid (Bauman *Ztschr. anal. chem.*, 1892 and others.)

The separation of nickel and cobalt, after the removal of manganese and zinc by hydrochloric acid, depends upon the solubility of nickel sulphide in a solution of sodium sulphide, the cobalt sulphide being insoluble in this reagent. (Villiers *compt. rend.*, 119, 1263, and 120, 46.) The sulphides of the two metals are dissolved in aqua regia and the greater part of the acid expelled. The solution is diluted and a slight excess of tartaric acid is added to prevent precipitation of the two metals by sodium hydroxide, which is next added in great excess. Hydrogen sulphide is now passed through the hot solution till no further precipitation occurs. Cobalt sulphide is precipitated and the nickel sulphide is held in solution by the sodium sulphide. The presence of a trace of nickel is indicated by the deep brown or black color which it imparts to the solution. The nickel sulphide is precipitated from this solution by the addition of dilute hydrochloric acid.

The following is an outline of the treatment: To a solution of the metals of the iron group add ammonium chloride and ammonium hydroxide, warm, and filter. Boil the precipitated iron, aluminum, and chromium hydroxides with sodium hydroxide, filter, acidify the filtrate, and add ammonium hydroxide. A white precipitate indicates aluminum. Boil the residue of iron and chromium hydroxides with sodium hydroxide and a few cubic centimeters of hydrogen peroxide. Filter; a yellow solution indicates chromium. Acidify filtrate with acetic acid and add lead acetate. A yellow precipitate indicates chromium. Dissolve the residue of iron hydroxide in hydrochloric acid and add potassium ferrocyanide. A blue precipitate indicates iron.

To the filtrate from iron, aluminum and chromium hydroxides add freshly prepared ammonium sulphide, heat, and filter. Wash the precipitate with cold dilute hydrochloric acid to dissolve manganese and zinc and treat the washings as usual for these two metals. Dissolve the residue of nickel and cobalt sul-

phides, left after washing with hydrochloric acid, in aqua regia, expel nearly all the acid, dilute, and add slight excess of tartaric acid, and then very great excess of sodium hydroxide. Boil and pass hydrogen sulphide through till no further precipitation occurs, filter immediately. Test the precipitate for cobalt by borax bead. The presence of nickel in the filtrate is indicated by its deep brown or black color. If nickel be absent the filtrate will be yellow or colorless.

If nickel be present add dilute hydrochloric acid to filtrate, filter, and test the precipitate for nickel by borax bead.

The ammonium sulphide should be prepared as recently as possible, as an excess of sulphur in solution causes the solution of a portion of the nickel sulphide.

## THE PROTEIDS OF BARLEY.<sup>1</sup>

BY THOMAS B. OSBORNE.

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THE proteids of barley have received little attention on the part of chemists. Mulder<sup>2</sup> states that this grain contains six per cent. of albumin and plant-gelatin; the latter was obtained by extracting barley-meal with hot alcohol, cooling the resulting solution and treating the deposited substance with ether. The composition of this body he gave as follows:

	1	2
Carbon .....	54.93	54.75
Hydrogen .....	7.11	6.99
Nitrogen .....	15.71	15.71
Sulphur .....	0.57	0.62
Oxygen .....	21.68	21.93
	<u>100.00</u>	<u>100.00</u>

v. Bibra<sup>3</sup> names albumin, plant-gelatin, and casein as constituents of barley but gives no particulars concerning these bodies further than that they all contain on the average 15.5 to 15.6 per cent. of nitrogen.

Kreusler made an investigation of the proteids of barley, the

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1894.

<sup>2</sup> Phys. Chem., I, 306-308.

<sup>3</sup> Die Getreidearten u. das Brod. Nürnberg, 1860, p. 304.

results of which are given by Ritthausen.<sup>1</sup> Kreusler employed coarsely ground meal and finely ground flour, the latter yielding purer preparations, the results being otherwise the same.

He states that the aqueous extract of the ground seed contains an albumin coagulated by boiling and of the following composition:

Carbon .....	52.86
Hydrogen .....	7.23
Nitrogen .....	15.75
Sulphur.....	1.18
Oxygen .....	22.98
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	100.00

The extract made with seventy-five per cent. alcohol contains, according to Kreusler, three proteids: gluten-casein, gluten-fibrin, and mucedin.

The gluten-casein separates on cooling the hot alcoholic extract, and when purified by boiling with dilute alcohol and fractionally precipitated from solution in acetic acid has the composition stated below.

1, is not corrected for ash and represents the first precipitation from a turbid solution.

2, is the second precipitation from a clear solution and is corrected for ash.

The cold alcoholic extract contains gluten-fibrin and mucedin.

The composition of these Kreusler gives as follows:

	Gluten-casein.		Gluten-fibrin.		Mucedin.	
	1.	2.	From meal.	From flour.	From meal.	From flour.
Carbon ....	53.84	53.25	55.23	54.55	53.19	53.97
Hydrogen ...	7.16	7.13	7.24	7.27	6.65	7.03
Nitrogen ....	16.63	....	15.49	15.70	16.14	16.98
Sulphur } ...	....	....	22.04	22.48	24.02	{ 0.68
Oxygen }						{ 21.34
						<hr/>
						100.00

These proteids were supposed to be the same as those similarly named and described by Ritthausen as occurring in the wheat kernel.

So far as the writer has been able to learn the preceding summary includes all that has been published hitherto in regard to the proteids of the barley kernel that is now worthy of notice.

<sup>1</sup> Die Eiweisskoerper, etc., Bonn, 1872, p. 103.



My preliminary examination of barley-meal showed that the seeds contain proteid matters soluble in water, in sodium chloride solutions, and in alcohol, and that after complete extraction with all these reagents there remains a considerable quantity of proteid which can be partly extracted by dilute potash solutions, but the greater part of which is insoluble in any reagent hitherto applied.

The material employed consisted of meal made from two-rowed barley and of a very white barley flour kindly furnished by the Health Food Co., of New York, both of which yielded proteids of the same composition and properties, the preparations derived from the flour, however, being less contaminated with coloring matter than those derived from the meal made from the entire grain, including the ground husk, which was so closely adherent, as to render its removal in the laboratory impossible.

#### PROTEIDS SOLUBLE IN WATER. LEUCOSIN. PROTEOSE.

As an aqueous extract of any seed, is in reality a dilute saline solution, owing to the salts extracted from the seed, and as the proteid matter soluble in alcohol dissolves to a slight extent in very dilute saline solutions, the proteids properly soluble in water were obtained by extracting the meal with sodium chloride solutions, dialyzing away the salts and filtering off the proteid that thereby precipitated. In this way the proteid matter, soluble in pure water, which had been extracted from the meal was obtained in solution by itself. Three kilos of barley, ground to a fine meal, were treated with nine liters of ten per cent. salt solution, applied in successive portions, the bran being removed by washing on a coarse cloth. The starch and other suspended matter was allowed to settle out and the extract was filtered clear. This solution was then saturated with ammonium sulphate and the precipitate produced, after filtering out, was treated with ten per cent. salt solution. The resulting liquid was filtered clear and dialyzed for five days. The globulin that separated in this process was collected on a filter, the solution was returned to the dialyzer for three days longer, and the very small additional amount of substance that separated was filtered out. The clear solution was then heated in a water-bath to 65°, the water of the bath not exceeding 70°. After an hour the coagulum was filtered

out, washed with warm water, alcohol, and ether, and dried over sulphuric acid. This preparation, 1, weighed 4.15 grams and when dried at 110° had the following composition:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 1.*

Carbon .....	53.04
Hydrogen .....	6.78
Nitrogen .....	16.84
Sulphur.....	1.42
Oxygen .....	21.92
	<hr/>
	100.00
Ash .....	0.29

Another preparation was made by treating two kilos of barley meal with ten per cent. sodium chloride solution, squeezing out in a press and repeating the process on the residue. The filtered extract was saturated with ammonium sulphate, the precipitate dissolved in dilute salt solution, subjected to dialysis and, when freed from chlorides, filtered and heated to 65° in a water-bath at 70°. The coagulum produced was washed thoroughly with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 2, weighed two and three-tenths grams and, when dried at 110°, had the following composition:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 2.*

Carbon .....	52.67
Hydrogen .....	6.77
Nitrogen .....	16.41
Sulphur }	24.15
Oxygen }	
	<hr/>
	100.00
Ash.....	0.31

As this body separated slowly when its solutions were heated to 65° it was thought possible that more than one albumin was present which, if a fact, might be shown by analysis of preparations, precipitated in successive fractions.

Accordingly six kilos of barley-meal were extracted with ten per cent. salt solution and the clear filtered extract saturated with ammonium sulphate. The precipitate produced was dissolved in brine and the solution, after filtering clear, was dialyzed until all the globulin had precipitated. It was then again filtered clear and in order to obtain a concentrated solution the filtrate

was saturated with ammonium sulphate, the precipitate formed was dissolved in water, and this solution was filtered clear and dialyzed. After six days only a very little more globulin had separated, which was filtered out, and a portion of the clear solution was tested carefully for its coagulation point. When slowly heated in a double water-bath it became faintly turbid at 39° and but very little more so at 49°. The turbidity then rapidly increased, flocks appearing at 56°. After heating at 56° for twenty minutes the solution was filtered and again heated. Turbidity occurred at 50° and flocks formed at 60°. After heating to 65° and holding at this temperature for some time the solution was filtered and again heated. Thereupon the turbidity took place at 70° and a very few flocks formed at 74°. The solution still had a just detectable acid reaction. The entire solution was then heated with great care to precisely 56° in a large water-bath, the temperature of which did not exceed 57°. After keeping at this temperature for an hour the coagulum was filtered out, washed with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 3, weighed 0.36 gram and contained, when dried, without correction for ash, 16.48 per cent. of nitrogen.

The filtrate from preparation 3, was then heated to just 60° for three hours, and the second coagulum filtered off and treated as the first had been. This preparation, 4, weighed four-tenths gram and contained, without correcting for ash, 16.74 per cent. of nitrogen. Another part of this same extract, after freeing from globulin as above described, was dialyzed into alcohol for three days, whereby the solution was concentrated and the proteid partly precipitated. In order to separate the albumin from any proteose thrown down with it, the precipitate produced by alcohol-dialysis was digested with absolute alcohol for three days longer and then washed thoroughly with water. A considerable part of the albumin was thus rendered insoluble in water, and after being further washed with absolute alcohol and ether, was dried over sulphuric acid and found to weigh 0.51 gram. This preparation, 5, contained 16.30 per cent. of nitrogen without correcting for ash.

Another preparation of albumin was made in the same way, in

order to obtain a larger quantity for complete analysis. Six kilos of barley flour were mixed with twenty-eight liters of ten per cent. salt solution and seventeen liters of clear filtrate obtained, which was saturated with ammonium sulphate. The precipitate produced was dissolved as far as possible in ten per cent. salt solution, filtered clear, and in order to reduce the volume of the solution it was saturated with ammonium sulphate, the precipitate dissolved in 1000 cc. of water, and dialyzed until entirely free from globulin. The solution was then filtered and dialyzed into alcohol. After being concentrated, absolute alcohol was added and the precipitate filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. This preparation, 6, weighed four and one-tenth grams. It was then digested with water and the insoluble matter washed thoroughly with water, alcohol, and ether, dried over sulphuric acid, and had the following composition when dried at 110°:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 6.*

Carbon .....	52.71
Hydrogen .....	6.78
Nitrogen .....	16.93
Sulphur.....	1.51
Oxygen .....	22.07
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	100.00
Ash .....	0.50

SUMMARY OF ANALYSES OF COAGULATED BARLEY ALBUMIN—LEUCOSIN.

	1.	2.	3. <sup>1</sup>	4. <sup>1</sup>	5. <sup>2</sup>	6. <sup>3</sup>	Average
Carbon.....	53.04	52.67	....	....	..	52.71	52.81
Hydrogen..	6.78	6.77	....	....	....	6.78	6.78
Nitrogen...	16.84	16.41	16.48	16.74	16.30	16.93	16.62
Sulphur ...	1.42	24.15	....	....	....	1.51	1.47
Oxygen....	21.92					22.07	22.32
	<hr/>	<hr/>				<hr/>	<hr/>
	100.00	100.00				100.00	100.00

If this proteid be compared with the leucosin<sup>4</sup> obtained from the wheat and rye kernels, it will be seen that the three are almost identical in composition.

<sup>1</sup> Not corrected for ash.

<sup>2</sup> Not corrected for ash; coagulated by alcohol.

<sup>3</sup> Coagulated by alcohol.

<sup>4</sup> Report of the Connecticut Agricultural Experiment Station, 1893, p. 179.

	LEUCOSIN.		
	Wheat.	Rye.	Barley.
Carbon.....	53.02	52.97	52.81
Hydrogen.....	6.84	6.79	6.78
Nitrogen.....	16.80	16.66	16.62
Sulphur.....	1.28	1.35	1.47
Oxygen.....	22.06	22.23	22.32
	100.00	100.00	100.00

The aqueous extract of the barley kernel contains also a small quantity of one or more proteoses, but owing to the great difficulties encountered in attempting to separate these, no pure preparations have been obtained.

#### PROTEID SOLUBLE IN SODIUM CHLORIDE SOLUTION. EDESTIN.

The large amount of gum extracted from barley-meal by salt solution renders it very difficult to prepare the globulin in anything like a pure state. This difficulty is further increased by the readiness with which the globulin passes into the insoluble or albuminate condition and is thus lost for further purification. In only three cases was it possible to redissolve and reprecipitate this proteid in sufficient quantity for analysis. In all the extracts made, a considerable amount of globulin was precipitated by dialysis in the form of minute spheroids. So far as noticed, this globulin resembled, in all respects, that found in wheat and rye. It was readily and completely precipitated from salt solution by dialysis and also by adding acid. When dissolved in ten per cent. sodium chloride solution and heated, turbidity occurred at 90°, but no coagulum formed until the solution was boiled, and then only a small part of the dissolved substance separated.

Three kilos of barley-meal were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, and the resulting precipitate filtered out, dissolved in ten per cent. brine, and the insoluble matter removed by filtration after adding a *very* small quantity of two-tenths per cent. potash water in order to neutralize the slight acid reaction of the extract. The solution was then filtered clear and dialyzed for four days. The proteid separated in the form of small spheroids which were filtered out, washed with water, alcohol, and ether, and after drying over sulphuric acid found to weigh 4.02 grams. This

preparation was dissolved in ten per cent. salt solution and again submitted to dialysis. After the proteid had precipitated it was filtered out, washed with water, alcohol, and ether, and the final preparation, 7, when dried at  $110^{\circ}$ , had the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 7.*

Carbon .....	51.43
Hydrogen .....	6.71
Nitrogen .....	18.14
Sulphur } .....	23.72
Oxygen }	
	<hr/> 100.00
Ash .....	0.48

Again six kilos of barley flour were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, the resulting precipitate dissolved in salt solution and dialyzed. The precipitated globulin was again dissolved in ten per cent. salt solution and precipitated a second time by dialysis. One and nine-tenths grams of preparation 8 were obtained, having the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 8.*

Carbon .....	50.82
Hydrogen .....	6.76
Nitrogen .....	18.16
Sulphur } .....	24.26
Oxygen }	
	<hr/> 100.00
Ash .....	0.37

Another preparation was made in the same way, save that after dissolving the ammonium sulphate precipitate in salt solution, the proteids were again precipitated by saturation with ammonium sulphate and redissolved in brine, thus yielding a solution of smaller volume which was then dialyzed. After five days' dialysis, the chlorides having been removed, the precipitated globulin was treated in the usual manner and found to weigh 1.85 grams. This preparation, 9, had the following composition:



BARLEY GLOBULIN, EDESTIN, *Preparation 9.*

Carbon .....	50.40
Hydrogen .....	6.48
Nitrogen .....	18.00
Sulphur } .....	25.12
Oxygen }	
<hr/>	
	100.00
Ash .....	0.44

The foregoing analyses, although not showing the agreement to be desired, are on the whole sufficiently alike to warrant their publication, and for the sake of comparison they are here tabulated.

## BARLEY GLOBULIN, EDESTIN.

	7.	8.	9.	Average.
Carbon.....	51.43	50.82	50.40	50.88
Hydrogen .....	6.71	6.76	6.48	6.65
Nitrogen .....	18.14	18.16	18.00	18.10
Sulphur } .....	23.72	24.26	25.12	24.37
Oxygen }				
<hr/>		<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00

In view of the close resemblance in properties and similarity in composition it is the writer's opinion that this globulin is the same as that found in a large number of other seeds and previously described under the name edestin.<sup>1</sup> The following table affords a comparison of the composition of this proteid from its different sources.

## EDESTIN.

	Wheat.	Maize.	Hemp-seed.	Castor-bean.	Squash-seed.	Flax-seed.	Cotton-seed.	Rye.	Barley.
C....	51.03	51.71	51.28	51.31	51.66	51.48	51.71	51.19	50.88
H ...	6.85	6.85	6.84	6.97	6.89	6.94	6.86	6.74	6.65
N....	18.39	18.12	18.84	18.75	18.51	18.60	18.64	18.19	18.10
S ....	0.69	0.86	0.87	0.76	0.88	0.81	0.62	23.88	24.37
O ....	23.04	22.46	22.17	22.21	22.06	22.17	22.17		
<hr/>		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

On comparing the above analyses it will be seen that the preparations obtained from the cereals show the greatest deviation from the average of these figures. This is unquestionably due to the fact that in these seeds this substance is present in small

<sup>1</sup> Report Connecticut Agricultural Experiment Station, 1893, pp. 179 and 216.

quantity and is associated with other bodies so that it has been impossible to prepare it from them in a state of perfect purity.

PROTEID SOLUBLE IN DILUTE ALCOHOL. HORDEIN.

After extracting 500 grams of barley-meal with brine the residue was treated with alcohol added in sufficient quantity to form with the water retained by the meal, an alcohol of approximately seventy-five per cent. After digesting a short time, the meal was squeezed out and again treated with seventy-five per cent. alcohol, and pressed out. The united alcoholic extracts were then filtered clear, concentrated to small volume on a water-bath, cooled, and the proteid thus separated washed thoroughly by kneading with distilled water. The separated substance now presented every appearance of gliadin, the proteid similarly obtained from wheat and rye. It was dissolved in a little dilute alcohol in which it was very readily soluble with the exception of a slight residue of coagulated proteid which rendered filtration extremely difficult. The solution was then precipitated by pouring into absolute alcohol and the precipitate digested with absolute alcohol, rubbed to a powder while still moist with alcohol, and treated with ether. When dried over sulphuric acid this preparation, 10, weighed 4.54 grams, and when dried at 110° gave on analysis the following results:

BARLEY PROTEID, *Preparation 10.*

	I.	II.	Average.
Carbon.....	53.83	53.93	53.88
Hydrogen.....	6.72	6.92	6.82
Nitrogen.....	17.32	....	17.32
Sulphur } .....	....	....	21.98
Oxygen }			
			100.00
Ash .....			0.22

Another extract was made by treating 500 grams of barley-meal with three liters of alcohol of nine-tenths specific gravity applied directly to the freshly ground meal. The extract, which had a red-brown color, was squeezed out in a press and concentrated to about one-eighth of its volume. After standing overnight the mother-liquor was poured off from the proteid which had separated in a firm mass on the bottom of the dish.



This was then dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. The resulting precipitate was washed with absolute alcohol, digested with ether, dried over sulphuric acid, and found to weigh 12.3 grams. This preparation, 11, when dried at 110°, had the following composition:

BARLEY PROTEID, *Preparation 11.*

Carbon .....	53.78
Hydrogen .....	6.51
Nitrogen .....	17.27
Sulphur.....	0.95
Oxygen .....	21.49
	<hr/>
	100.00
Ash .....	0.19

The remainder of preparation 11 was then dissolved in dilute alcohol and, after filtering clear, poured into distilled water and precipitated by adding a few drops of sodium chloride solution. This substance was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After treating with ether and drying at 110°, this preparation, 12, was analyzed with the following results:

BARLEY PROTEID, *Preparation 12.*

Carbon .....	53.78
Hydrogen .....	6.82
Nitrogen .....	17.16
Sulphur .....	0.93
Oxygen .....	21.31
	<hr/>
	100.00
Ash .....	0.86

Three kilos of barley-meal were treated with ten per cent. salt solution and washed on a coarse cloth until only the bran and larger particles of meal remained. This residue was then extracted with alcohol of nine-tenths specific gravity, yielding a deep red solution, which was filtered through animal charcoal; but only a part of the coloring-matter was removed. The clear solution was next concentrated on a water-bath, poured into absolute alcohol, and the resulting precipitate digested with absolute alcohol and treated with ether, giving preparation 13, weighing thirty grams and, when dry, having the following composition:

BARLEY PROTEID, *Preparation 13.*

	I.	II.	Average.
Carbon.....	53.80	53.70	53.75
Hydrogen.....	....	6.78	6.78
Nitrogen.....	17.48	17.33	17.41
Sulphur .....	0.93	....	0.93
Oxygen .....	....	....	21.13
			100.00
Ash .....			0.25

A portion of the solution from which preparation 13 had been obtained was precipitated separately by pouring into strong alcohol and adding a few drops of salt solution. The precipitate was treated in the usual manner and gave a preparation, 14, containing much less coloring-matter than the preceding and having the following composition :

BARLEY PROTEID, *Preparation 14.*

Carbon .....	54.32
Hydrogen .....	6.74
Nitrogen .....	17.13
Sulphur } .....	21.81
Oxygen }	
	100.00
Ash .....	1.43

The starchy portion of the barley-meal which had been washed through the cloth, as described, was thoroughly extracted with salt solution and then with dilute alcohol, the extraction being repeated until the proteid was completely removed. The united extracts were filtered and concentrated to two-thirds their volume by distillation when the solution was poured into a dish and the evaporation continued. The proteid separated as a skin on the surface of the liquid and as a solid mass on the bottom of the dish. When reduced to about one-half the volume of the original liquid the hot mother-liquor was decanted from the separated proteid which formed a tough mass of a pink color. This was washed with water and redissolved in dilute alcohol, giving a deep red solution which was poured into absolute alcohol and the mass of substance that separated was cut up with scissors into small pieces and digested with absolute

alcohol and with ether. When dried over sulphuric acid this preparation, 15, was pinkish in color and weighed thirty grams. Dried at 110° and analyzed the following results were obtained :

BARLEY PROTEID, *Preparation 15.*

Carbon .....	54.00
Hydrogen .....	6.72
Nitrogen .....	17.49
Sulphur } .....	21.79
Oxygen } .....	
	<hr/>
	100.00
Ash .....	0.95

The mother-liquor decanted from preparation 15, was still further concentrated and allowed to cool over night. Only a little substance separated which, however, was washed with water, redissolved in dilute alcohol, and precipitated by pouring into much distilled water to which a little salt had been added. On standing about thirty-six hours the milky solution cleared and the proteid was found in a transparent layer at the bottom of the vessel. After treating with absolute alcohol and ether and drying over sulphuric acid, preparation 16 was obtained weighing seven grams and having when dried, the following composition :

BARLEY PROTEID, *Preparation 16.*

Carbon .....	53.90
Hydrogen .....	6.63
Nitrogen .....	17.08
Oxygen } .....	22.39
Sulphur } .....	
	<hr/>
	100.00
Ash .....	0.23

As this proteid resembled gliadin so closely in its physical and chemical properties it seemed important to subject it to very thorough fractional precipitation in order to determine whether it was a mixture of gliadin with another body or a new, distinct proteid. Another extract was made by treating three kilos of freshly ground barley-meal with ten per cent. salt solution, squeezing out in a press, and treating the residue again in the same way. The meal residue was then mixed with alcohol in

quantity sufficient to make, with the water retained by the meal an alcohol of about forty per cent. After squeezing out the liquid, alcohol was again added to the residual meal sufficient to increase the strength of the solvent to seventy-five per cent. After digesting for some time the extract was squeezed out and found less colored than the first dilute alcohol extract. This second extract was concentrated by distillation to small volume and cooled giving a deposit of proteid much whiter than any previously made. The mother-liquor from this precipitate was poured into absolute alcohol and a second precipitate obtained. The two precipitates, when united, dehydrated in the usual way treated with ether, and dried over sulphuric acid, weighed twenty-two grams. Dried at  $110^{\circ}$  this substance had the following composition:

*BARLEY PROTEID, Preparation 17.*

Carbon .....	54.30
Hydrogen .....	6.67
Nitrogen .....	17.47
Sulphur .....	0.84
Oxygen .....	20.72
	<hr/>
	100.00

About eighteen grams of this preparation were dissolved in alcohol of 0.9 specific gravity and absolute alcohol was added until a considerable precipitate resulted, when the mixture was heated on a water-bath until the precipitate dissolved. The solution was then cooled and after standing some time the mother-liquor was decanted from the separated substance. The precipitate was marked I. The solution decanted from I, was further treated with absolute alcohol and a second precipitate I was obtained in the same way. The mother-liquor from II was mixed with a large quantity of absolute alcohol and, as the proteid did not separate, a few drops of salt solution were added and the resulting precipitate III filtered off and treated with absolute alcohol and ether in the usual manner.

In the first place, precipitate I was dissolved in a small quantity of seventy-five per cent. alcohol and absolute alcohol was added until the precipitate began to reappear. The whole was heated until the precipitate again dissolved whereupon the solution

tion was cooled. The substance which separated settled out leaving the solution milky. The mother-liquor was decanted from the small amount of deeply colored proteid which adhered to the bottom of the beaker, and this deposit was dissolved in a little seventy-five per cent. alcohol, treated with absolute alcohol, and the opalescent solution so produced mixed with a little ether. This gave a very small precipitate, almost black in color and very sticky. The solution decanted from this small deposit was treated with a drop of potassium acetate solution and the resulting precipitate, after washing with absolute alcohol and ether, dried over sulphuric acid. It formed a light pink powder, preparation 18, weighing 0.65 gram and when dry contained, ash-free, 16.60 per cent. of nitrogen. Its ash content was 1.04 per cent. The mother-liquor, decanted from the first precipitation of 18, was treated with a drop of potassium acetate solution and the precipitate produced allowed to settle. After standing, the substance settled out and adhered to the bottom of the beaker in a solid mass, from which the clear supernatant solution was decanted. This solution after treatment with absolute alcohol yielded a precipitate which, washed with absolute alcohol and ether, and dried, formed preparation 19, weighing 1.79 grams and having the following composition:

BARLEY PROTEID, *Preparation 19.*

Carbon .....	53.85
Hydrogen .....	6.69
Nitrogen .....	17.22
Sulphur } .....	22.24
Oxygen }	
	100.00
Ash .....	0.40

The substance deposited after the addition of potassium acetate to the solution from which 19 was derived, was dissolved in seventy-five per cent. alcohol, absolute alcohol added to the solution, and the resulting precipitate dissolved by heating. On cooling, a part of the proteid separated and after this had settled, the liquid was decanted and mixed with absolute alcohol, and on treating the precipitate in the usual manner preparation 20 was obtained, which when dried weighed 1.18 gram and gave the following results on analysis:

BARLEY PROTEID. *Preparation 20.*

Carbon .....	54.33
Hydrogen .....	6.81
Nitrogen .....	16.93
Sulphur } .....	21.93
Oxygen } .....	
	100.00
Ash.....	0.58

The substance deposited by cooling the solution from which 20 was obtained was only partly soluble in dilute alcohol. It was accordingly treated with seventy-five per cent. alcohol and allowed to stand until the insoluble matter had settled out. The clear liquid was then decanted and completely precipitated with absolute alcohol. The separated substance was washed with absolute alcohol and ether and when dry weighed 0.81 gram. This preparation, 21, contained, ash-free, 16.65 per cent. of nitrogen and 0.32 per cent. of ash. The insoluble matter just described, after washing by decantation with seventy-five per cent. alcohol, was treated in the usual manner and yielded preparation 22, weighing 1.56 grams and having the following composition :

BARLEY PROTEID. *Preparation 22.*

Carbon .....	53.91
Hydrogen .....	6.77
Nitrogen .....	17.00
Sulphur } .....	22.32
Oxygen } .....	
	100.00
Ash.....	0.71

Precipitate II was dissolved in a little seventy-five per cent. alcohol and the solution mixed with absolute alcohol. The resulting precipitate (*a*) was dissolved by heating and the solution cooled, whereupon a part (*b*) of the proteid was precipitated. The supernatant solution was poured off, mixed with absolute alcohol, and this precipitate (*c*) which contained all the proteid remaining was dehydrated with absolute alcohol and washed with ether, giving preparation 23, weighing two and

two-tenths grams and having, when dry, the following composition :

BARLEY PROTEID. *Preparation 23.*

	I.	II.	Average.
Carbon.....	54.63	54.68	54.65
Hydrogen.....	6.62	6.50	6.56
Nitrogen .....	17.16	.....	17.16
Sulphur } .....	.....	.....	21.63
Oxygen } .....	.....	.....	.....
			100.00
Ash.....	.....	.....	0.32

The substance (*b*), deposited on cooling the solution as above described, was dissolved in seventy-five per cent. alcohol and partly precipitated by adding absolute alcohol. After redissolving the precipitate by the application of heat, the solution was cooled and allowed to stand some time to deposit the precipitate which formed. The liquid was then decanted and the separated substance treated with absolute alcohol and ether, yielding preparation 24, weighing 3.11 grams and having the following composition after drying at 110°.

BARLEY PROTEID. *Preparation 24.*

Carbon .....	54.27
Hydrogen.....	6.67
Nitrogen .....	17.39
Sulphur } .....	21.67
Oxygen } .....	.....
	100.00
Ash.....	0.32

To the solution from which 24 separated, absolute alcohol was added in considerable quantity and the proteid thus thrown down was dehydrated with absolute alcohol and washed with ether. When dried this preparation, 25, weighed 0.87 gram and, without correction for ash, contained 17.28 per cent. of nitrogen.

Precipitate III was treated with absolute alcohol and with ether, and dried over sulphuric acid. It weighed 1.63 grams and its composition after complete drying was :



BARLEY PROTEID. *Preparation 26.*

Carbon .....	53.39
Hydrogen.....	7.02
Nitrogen .....	17.49
Sulphur } .....	22.10
Oxygen } .....	
	100.00
Ash.....	0.59

If these figures are compared it will be seen that no fractional separation has been effected, the variations in the results being no greater than in the preparations previously described. Preparation 18 is low in nitrogen, but this is doubtless due to its containing nearly all the impurities precipitable from the solution. Preparation 21 is also low in nitrogen but this was the most colored of all the preparations and as it was also small in quantity the accuracy of the analysis could not be confirmed. Excluding these two preparations the results agree fairly and are shown by the following table :

## SUMMARY OF THE PRECEDING FRACTIONAL PRECIPITATES.

	19.	20.	22.	23.	24.	25.	26.	Original substance 17.
Carbon ...	53.85	54.33	53.91	54.65	54.27	....	53.39	54.30
Hydrogen	6.69	6.81	6.77	6.56	6.67	....	7.02	6.67
Nitrogen..	17.22	16.93	17.00	17.16	17.39	17.28	17.49	17.47
Sulphur }	22.24	21.93	22.32	21.63	21.67	....	22.10	21.56
Oxygen }								
	100.00	100.00	100.00	100.00	100.00		100.00	100.00
Weight ...	1.79	1.18	1.56	2.2	3.11	0.87	1.63	18.00

As all the preceding preparations were made by extracting barley-meal which contained a large quantity of bran, they were much contaminated with coloring-matter.

In order to obtain products free from color 880 grams of finely ground "pearled barley" (a commercial preparation of barley made by rubbing off the outer coat of the grain), were treated with salt solution, and after squeezing out the excess of liquid the residue was digested with seventy-five per cent. alcohol. The extract was then filtered, concentrated to small volume, cooled, and the mother-liquor decanted from the separated proteid. This was then dissolved in dilute alcohol, the solution



poured into distilled water, and the proteid thrown down by adding a little salt. The precipitate was again dissolved in a small amount of dilute alcohol and reprecipitated by pouring into absolute alcohol, digested with absolute alcohol for some time, then with ether, dried over sulphuric acid, and found to weigh eight grams. This preparation, 27, was pure white and had the following composition when thoroughly dried :

BARLEY PROTEID. *Preparation 27.*

Carbon .....	54.37
Hydrogen .....	6.81
Nitrogen .....	17.33
Sulphur .....	0.88
Oxygen.....	20.61
	<hr/>
	100.00
Ash.....	0.48

Another preparation was made by extracting six kilos of barley flour with salt solution and then treating the residue with alcohol added in sufficient quantity to make with the water of the brine, which still adhered to the meal, as nearly as possible seventy-five per cent. alcohol. After standing over night the extract was filtered off, concentrated to about one-third its original volume, and cooled slightly. The proteid that now separated out from the hot solution was removed from the liquid, rinsed with water, dissolved in a very little dilute alcohol to a thick syrup, and reprecipitated by pouring into absolute alcohol. The substance was then cut up into small pieces and digested with absolute alcohol and also with ether. When dried over sulphuric acid seventy-eight grams of a pure white preparation were obtained. Twenty-five grams of this were then dissolved in seventy-five per cent. alcohol and the clear solution poured into a large volume of distilled water. A part of the substance separated, leaving the liquid milky. The milky solution was decanted from the separated substance and the latter was washed with water in which some of it dissolved. The turbid liquid and washings were united and precipitated with a little salt solution. After standing over night the proteid separated as a transparent viscid liquid on the bottom of the vessel in the same way as gliadin does under similar conditions. After decanting the supernatant

liquid the deposit was dissolved in dilute alcohol and precipitated by pouring its solution into absolute alcohol. The separated proteid was then digested with absolute alcohol and with ether and dried over sulphuric acid. A pure white preparation, 28, resulted, which when dried at  $110^{\circ}$  had the following composition :

BARLEY PROTEID. *Preparation 28.*

Carbon .....	54.02
Hydrogen.....	6.79
Nitrogen .....	17.38
Sulphur .....	0.84
Oxygen.....	20.97
	<hr/>
	100.00
Ash.....	1.00

The mass which separated on pouring the alcoholic solution into water, as above described, was dissolved in seventy-five per cent. alcohol and, as it contained a little insoluble proteid which rendered filtration impossible, the solution was allowed to stand over night. The clear supernatant solution was then poured off and concentrated to about one-third of its volume and cooled. The proteid which separated was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After thorough dehydration with absolute alcohol and digestion with ether, the substance was dried over sulphuric acid and yielded preparation 29, which was white in color and weighed 5.46 grams. This substance, when dried, had the following composition :

BARLEY PROTEID. *Preparation 29.*

	I.	II.	Average.
Carbon.....	54.48	54.54	54.51
Hydrogen.....	6.70	6.79	6.75
Nitrogen .....	17.22	17.18	17.20
Sulphur } .....	21.60	21.49	21.54
Oxygen } .....			
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash.....			0.32

Another preparation was made without heating, by pouring a part of the original extract from which preparations 28 and 29 were derived into a large amount of distilled water and allowing

the separated substance to deposit. After some time this settled and the supernatant liquid was poured off, the precipitate washed with water, dissolved in cold dilute alcohol, and the solution poured into absolute alcohol. The precipitate produced was digested with absolute alcohol and then with ether and dried over sulphuric acid, yielding a pure white preparation having, when dry, the following composition:

BARLEY PROTEID. <i>Preparation 30.</i>	
Carbon.....	54.23
Hydrogen.....	6.83
Nitrogen .....	17.27
Sulphur .....	0.75
Oxygen.....	20.92
	<hr/>
	100.00
Ash.....	0.17

In order to obtain a larger quantity of a colorless preparation, five kilos of barley flour were treated with 10.5 liters of seventy-five per cent. alcohol, and after standing some time the extract was filtered off and six liters of clear solution obtained. This was then concentrated to one-third its volume and rapidly cooled. The proteid separated as a bulky plastic mass, which, after decanting the mother-liquor, was macerated with about 500 cc. of distilled water, the washings were poured off, and the mass of proteid dissolved in 500 cc. of seventy-five per cent. alcohol, yielding a solution of a pale yellowish brown tint. This solution was poured in a thin stream into a quantity of distilled water, and the separated proteid, after removal from the liquid, was again dissolved in seventy-five per cent. alcohol, and the perfectly clear solution poured in a small stream into a large quantity of absolute alcohol. As the soluble salts had been almost completely removed the proteid did not separate even after admixture of 800 cc. of absolute ether. Three or four cc. of salt solution were therefore added to the milky liquid, and an immediate precipitate resulted which rapidly settled, leaving the solution clear and free from proteid. This mixture of absolute alcohol and ether retained all the fat present in the proteid before precipitation, and also some coloring-matter, the liquid being yellow. The solution was decanted and the voluminous precipitate treated with successive portions of absolute alcohol, and

obtained as a snow-white granular substance, weighing, when dried over sulphuric acid, ninety-three grams. This preparation, 31, had the following composition when dried at 110°:

BARLEY PROTEID. *Preparation 31.*

	I.	II.	Average.
Carbon.....	54.18	54.31	54.25
Hydrogen.....	6.98	6.65	6.82
Nitrogen.....	17.20	17.30	17.25
Sulphur.....	0.84	....	0.84
Oxygen.....	....	....	20.84
			100.00
Ash.....			0.09

In order to make certain that this proteid, which so closely resembled gliadin in every respect but composition, was not the substance contaminated with fat, a portion of this preparation was ground to a very fine powder and washed for a long time with hot ether in an extraction apparatus. Only a trace of substance was removed by this treatment, and the proteid after drying, had the same composition as before, as the following figures show:

BARLEY PROTEID. *Preparation 32.*

Carbon.....	54.20
Hydrogen.....	6.58
Nitrogen.....	17.07
Sulphur.....	0.91
Oxygen.....	21.24
	100.00
Ash.....	0.25

Another portion of 31 was dissolved in two-tenths per cent. potash water, yielding a clear solution, which was precipitated by neutralization with two-tenths per cent. hydrochloric acid. The precipitate was washed with water, dehydrated with absolute alcohol, washed with ether, and analyzed with the following results:

BARLEY PROTEID. *Preparation 33.*

Carbon.....	54.21
Hydrogen.....	6.87
Nitrogen.....	17.12
Sulphur.....	0.76
Oxygen.....	21.04
	100.00
Ash.....	0.25

Preparation 31 was then subjected to fractional precipitation in order to make sure that it was not a mixture of two or more

proteids. Twenty-five grams were dissolved in 300 cc. of alcohol of 0.865 sp. gr. by heating on a water-bath, and the solution was quickly cooled. After adding a few drops of ten per cent. salt solution the most of the proteid separated in a coherent mass, leaving the liquid clear. After decantation, the residue was treated in the same way again, the decanted solutions being united. The residue was again dissolved and absolute alcohol added to the hot solution until a considerable precipitate resulted, when it was heated until clear and then cooled. A few drops of salt solution were then added and the proteid precipitated, leaving the solution slightly milky. This liquid was joined to the two solutions from which the proteid had been previously separated, and a little more salt solution added to the mixture, thereby precipitating the remainder of the dissolved proteid. After decanting the liquid from the separated substance the latter was treated with absolute alcohol and gave preparation 34, representing the fraction soluble in the strongest alcohol and having, when dry, the following composition:

BARLEY PROTEID. *Preparation 34.*

Carbon .....	54.32
Hydrogen.....	6.78
Nitrogen.....	17.02
Sulphur .....	0.94
Oxygen.....	20.94
	<hr/>
	100.00
Ash.....	0.21

The proteid, which had been precipitated during the preparation of this substance as just described, was dissolved in alcohol of 0.865 sp. gr., and the solution cooled rapidly by immersing in cold water. When a part of the substance had separated the solution was decanted and the separated substance treated with absolute alcohol. Preparation 35 was thus obtained, which gave the following figures on analysis:

BARLEY PROTEID. *Preparation 35.*

Carbon .....	54.47
Hydrogen.....	7.01
Nitrogen .....	17.15
Sulphur .....	0.74
Oxygen.....	20.63
	<hr/>
	100.00
Ash.....	0.43

The above preparation represented the portion least soluble in strong alcohol. The solution decanted from this preparation was precipitated with absolute alcohol and a few drops of salt solution, and the resulting precipitate, after the usual treatment, yielded preparation 36, having the following composition:

BARLEY PROTEID. *Preparation 36.*

Carbon .....	54.37
Hydrogen.....	6.81
Nitrogen .....	17.30
Sulphur .....	0.84
Oxygen.....	20.68
	<hr/>
	100.00
Ash.....	0.38

The following table includes all analyses of the preparations which were free from coloring-matter.

HORDEIN. - BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	27.	28.	29.	30.	31.	32.
Carbon .....	54.37	54.02	54.51	54.23	54.25	54.20
Hydrogen.....	6.81	6.79	6.75	6.83	6.82	6.58
Nitrogen .....	17.33	17.38	17.20	17.27	17.25	17.07
Sulphur.....	0.88	0.84	21.54	0.75	0.84	0.91
Oxygen.....	20.61	20.97		20.92	20.84	21.24
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00
		33.	34.	35.	36.	Average.
Carbon.....		54.21	54.32	54.47	54.37	54.29
Hydrogen .....		6.87	6.78	7.01	6.81	6.80
Nitrogen .....		17.12	17.02	17.15	17.30	17.21
Sulphur .....		0.76	0.94	0.74	0.84	0.83
Oxygen .....		21.04	20.94	20.63	20.68	20.87
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		100.00	100.00	100.00	100.00	100.00

This body differs essentially from all the well-defined plant proteids now known. As it appears to be characteristic of barley, I propose to adopt for it the latterly disused name *hordein*, which was first applied about 1870 by Proust<sup>1</sup> and ten years later by Hermstädt<sup>2</sup> to certain products of their attempts to isolate the proximate principles of this cereal.

Hordein appears to have been obtained nearly pure from bar-

<sup>1</sup> Ann. chim. phys., 5, 337.

<sup>2</sup> J. tech. Chem., 12, 46.

ley flour by Kreusler, as shown by the following comparison of his analysis with the average above given.

## BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	Kreusler.	Osborne.
Carbon....	53.97	54.29
Hydrogen.....	7.03	6.80
Nitrogen .....	16.98	17.21
Sulphur .....	0.68	0.83
Oxygen.....	21.34	20.87
	100.00	100.00

Ritthausen regarded this proteid as identical with the mucedin believed by him to occur in wheat and rye, but which, as my investigations prove, does not exist in those grains.

Toward water my different preparations of hordein behave somewhat differently. Preparations dried over sulphuric acid and still retaining a little alcohol dissolve in cold water to a greater or less extent according to the amount of alcohol present. When dried completely at  $110^{\circ}$ , so that all the alcohol is removed, very little hordein dissolves in cold water and slightly more on raising the temperature. Solutions thus made with hot water do not precipitate on cooling or coagulate on boiling although they give no inconsiderable precipitates on adding salt. A large number of preparations of this proteid and of wheat gliadin were thus tested and compared under similar conditions. The gliadin showed variations in solubility in the same way as the barley proteids, but throughout was much more soluble than the latter, yielding solutions with warm water which were precipitated by cooling. As drying at  $110^{\circ}$  tends to render more or less of these proteids insoluble in seventy-five per cent. alcohol it is not possible to say definitely whether the difference was due to original difference in properties of the two proteids tested or to the drying. It is the opinion of the writer that the hordein of barley is decidedly less soluble in water than the gliadin of wheat.

Toward alcohol the hordein behaves, so far as could be detected, exactly like gliadin. In very dilute acids and alkalis it is readily soluble and is precipitated by neutralization. Dissolved in concentrated hydrochloric acid a beautiful crimson color is produced similar to that given by gliadin under like



conditions. With a warm mixture of equal volumes of water and concentrated sulphuric acid a red color is given by hordein, not a purple red as by gliadin.

The most marked difference between hordein and gliadin is in composition, since hordein contains one and a half per cent. more carbon, one and a half per cent. less nitrogen, and three-tenths per cent. less sulphur than gliadin.

In the extraction last described 5000 grams of barley flour were treated with 10.5 liters of alcohol, and the extract obtained measured six liters, which was equivalent to 57.1 per cent. of the whole solution employed. If we assume, as is very nearly true, that this was equal to a complete extraction of 57.1 per cent. of the flour, the proteid obtained was equivalent to all the alcohol-soluble proteid contained in 2855 grams of flour. In addition to the ninety-three grams of proteid above described, there was obtained a further quantity weighing, when thoroughly dried over sulphuric acid, 17.5 grams, thus making in all 110.5 grams. This quantity is 3.87 per cent. of the 2855 grams extracted. In order to confirm these figures 500 grams of barley flour were extracted with two liters of hot seventy-five per cent. alcohol, squeezed out in a press and the residual meal treated again in the same way with another liter of alcohol and the united extracts filtered clear and concentrated by evaporation. All the proteid contained in the solution separated on cooling and was washed with ether, then dehydrated with absolute alcohol, again digested with ether, and dried completely over sulphuric acid. Twenty and two-tenths grams of proteid were thus obtained equal to 4.04 per cent of the flour. We may therefore assume that this barley flour contained about four per cent. of the alcohol-soluble proteid, hordein.

#### PROTEID INSOLUBLE IN WATER, SALINE SOLUTIONS, AND ALCOHOL.

The proteids thus far described form only a part of the total proteids of the seed. One hundred grams of barley flour were extracted, first, with a large excess of five per cent. salt solution and then, repeatedly, with hot seventy-five per cent. alcohol. The residue, washed with absolute alcohol and thoroughly air-dried, weighed seventy-one grams and contained 1.07 per cent



of nitrogen. The air-dry flour, before extraction, contained 1.83 per cent. of nitrogen. The 100 grams of flour therefore contained 1.83 grams of nitrogen and the residue, after extraction, contained 0.76 grams. The nitrogen removed by the solvents therefore amounted to 58.3 per cent. of the whole.

If we assume that the nitrogen all belonged to proteid-matter containing seventeen per cent. of nitrogen, the flour included 10.76 per cent of proteids, of which 58.3 per cent. was soluble in the reagents used in extracting the proteids already described. We have therefore  $10.76 - 6.28 = 4.48$  per cent. of proteid unextracted. It was only possible to obtain this proteid by treating the residue with potash water. All attempts, however, to thus prepare it in quantity sufficient to yield preparations of even approximate purity resulted in complete failure.

The previous extraction of the flour to remove the proteids already described seemed to render, to a great extent, the remaining proteid insoluble in potash water and only insignificant precipitates resulted on neutralizing the extracts. The barley flour also contained a large quantity of gum which rendered the filtration of the alkaline extract very difficult, as this gum dissolved freely in potash water. As the proteids prepared from the barley flour are all so similar to those obtained from wheat flour it is most probable that this seed also contains a considerable quantity of proteid soluble only in dilute alkaline solutions, but, as in the case of rye, the writer was unable to obtain results of any value whatever in regard to it.

#### CONCLUSION.

The barley kernel contains :

I. Leucosin coagulating at  $52^{\circ}$ , which is the same as the album found in the wheat and rye kernels. Its composition, as shown by the average of six analyses, is:

Carbon.....	52.81
Hydrogen.....	6.78
Nitrogen .....	16.62
Sulphur .....	1.47
Oxygen.....	22.32
	<hr/>
	100.00

This substance forms about three-tenths per cent. of the seed.

II. A small quantity of proteose, the reactions and composition of which could not be definitely ascertained.

III. Edestin, a globulin which is the same as that found in the wheat and rye kernels and in a large number of other seeds. Its composition is approximately shown by the figures given below. Owing to the small amount of this body and the difficulty in preparing it, no perfectly pure preparations were obtained.

Carbon .....	50.88
Hydrogen.....	6.65
Nitrogen .....	18.10
Sulphur } .....	24.37
Oxygen } .....	
	100.00

This is the proteid commonly known as vegetable vitellin. It is precipitated from saline solutions by dilution and by dialysis, is not coagulated by heating below 90°, and above that temperature only partially. It is not precipitated by saturating its solution with sodium chloride, but is thrown down from saline solutions by adding acid.

IV. Hordein, a proteid insoluble in saline solutions, very slightly soluble in pure water, and extremely soluble in alcohol of about seventy-five per cent. This is the barley proteid described by Ritthausen as mucedin. It has almost the same physical and chemical properties as gliadin obtained from wheat and rye kernels but a different composition.

Carbon .....	54.29
Hydrogen.....	6.80
Nitrogen .....	17.21
Sulphur .....	0.83
Oxygen.....	20.87
	100.00

About four per cent. of the seed consists of this substance.

V. After extracting the barley flour with salt solution and with alcohol the residue still contained forty-two per cent. of the total nitrogen, corresponding to proteid-matter equal to about four and five-tenths per cent. of the flour. It was not possible to extract more than a very small amount of this residual pro-

teid with dilute potash water, as the treatment for removal of the other proteids rendered it insoluble, if it were not so already.

VI. The barley flour contained 1.83 per cent. of nitrogen, and if it be assumed that this all belonged to proteid-matter with seventeen per cent. of nitrogen, the flour would contain 10.75 per cent. of proteids. The barley accordingly contained about four and a half per cent. of insoluble proteid, four per cent. of hordein soluble in dilute alcohol, three-tenths per cent. albumin, and 1.95 per cent. of globulin and proteose.

### THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.<sup>1</sup>

BY H. C. SHERMAN.

Received April 13, 1895.

AS soon as the accuracy of the Kjeldahl method for the determination of nitrogen was generally recognized, attention was turned toward the discovery of some simple modification by which it could be made applicable in the presence of nitrates.

Asboth (*Chem. Centrbl.*, 1886) recommended the simple addition of benzoic acid to the decomposing mixture. It was soon found that this method was not sufficient.

The following year, two methods were brought before the Association of Official Agricultural Chemists, one by Mr. Scovell, the other by Mr. Farrington. The principal difference consisted in the use of salicylic acid with the sulphuric acid to fix the nitrogen oxides by the former, while phenol was used for the same purpose by the latter. Both used zinc dust as the reducing agent. The Scovell method was adopted and remains practically unchanged.

In 1890, the Association sanctioned the use of zinc sulphide as a reducing agent. In case of its use the acid mixture was to contain one gram of salicylic acid instead of two. The use of zinc dust with two grams salicylic acid was retained.

In 1892, sodium thiosulphate, which had been used for reducing nitrates in the Ruffle method, was adopted as a third reducing agent, and it was directed that five grams of the crystalized salt should be added "direct."

<sup>1</sup> Read before the Washington Section.

In 1893, the use of zinc sulphide was dropped, (because this reagent was likely to contain nitrogen) and a modification of the Gunning method was adopted. In the latter, five grams of thio-sulphate and one gram of salicylic acid were used with the same amount of potassium sulphate as in the plain method (ten grams). It was claimed that that all the reagents could be added with the substance, but further trials disproved this, and in 1894 the requirement of first mixing the substance with the acid mixture was made practically the same as in the modified Kjeldahl.

It has been the experience of the writer, and the amount of work which has been done by the Association, indicates that it is the same with others, that the determination of nitrogen in fertilizers containing nitrates is attended with greater difficulty than in those free from nitrogen in this form. In the hope of discovering whether this is due to any considerable extent to the official methods, and, if so, the reasons therefor, the following experiments were undertaken.

A set of four samples was first prepared, composed of the following materials:

No. 1, sodium nitrate, ammonium sulphate, potassium chloride, acid phosphate.

No. 2, sodium nitrate, bone phosphate, dried blood, ammonite, marl filler.

No. 3, sodium nitrate, tobacco stems, cottonseed-meal, castor pomace.

No. 4, sodium nitrate, dried fish, natural guano.

In each case all the materials, except the nitrate, were first mixed, ground to pass through a five-tenths mm. sieve, and air-dried. Nos. 1, 2, and 3 were then mixed again, and the percentage of nitrogen carefully determined by both the Kjeldahl and Gunning methods. The guano used in preparing No. 4 contained a small amount of nitric nitrogen, and could not be determined in this manner.

An air-dried sample of sodium nitrate was then ground to pass through the same sieve, and its nitrogen content determined by the silica fusion method. This sample was then carefully mixed with those above described in such proportions as to give to each the desired percentage of nitrogen. Nos. 1, 2, and 3 were cal-

culated to contain ten per cent., eight and one-half per cent., and eight and one-half per cent. respectively. No. 4 was expected to show about eight per cent. These percentages are as high as are likely to be found in ordinary mixed fertilizers.

The materials employed represent all the general classes of ingredients commonly used in this section, and since no one of them composed less than fifteen per cent. of the mixture in which it occurred, any effect which it might tend to produce would be almost sure to be noticeable in the result.

The results on these mixtures by the official methods are given in Table I.

TABLE I. PER CENT NITROGEN FOUND IN KNOWN MIXTURES.

No.	Calculated.	Modified Kjeldahl Zinc dust.	Modified Gunning.
1.....	10.00	9.93	9.80
2.....	8.50	8.51	8.50
3.....	8.50	8.48	8.50
4.....	...	8.12	8.08

Except in the case of No. 1, the figures given are the averages of two (and only two) determinations. The greatest difference between duplicates was 0.08 per cent.; the average difference 0.03 per cent.

Four determinations were made by each method on No. 1. These are given below.

The official methods as given on page 347 (Bul. 43, U. S. Dept. of Agr., Division of Chemistry) were followed closely with the following additional precautions.

1. In working the modified Kjeldahl method, the zinc dust was added through a funnel tube, very slowly, and with constant shaking. About two minutes is required to add the zinc dust in this way. After the first boiling, the flasks were allowed to cool somewhat before the mercuric oxide was added.

2. In the modified Gunning method, the boiling was continued about thirty minutes after the contents of the flask had become "nearly colorless."

To test these points determinations were made on Nos. 2, 3, and 4 without the precautions noted, but in every other way as above. The average results, together with those given above, are shown in Table II.

TABLE II. SHOWING EFFECT OF PRECAUTIONS NOTED ABOVE.

No.	Calculated.	Modified Kjeldahl:		Modified Gunning:	
		As above.	Zinc added in three to five portions and HgO at boiling heat.	As above.	Boiling stopped when nearly colorless.
2 .....	8.50	8.51	8.47	8.50	8.55
3 .....	8.50	8.48	8.46	8.50	8.36
4 .....	8.10 <sup>1</sup>	8.12	8.05	8.08	7.95
Av.	8.37	8.37	8.33	8.36	8.22

It is noticeable that the duplicates agreed about as closely as when the precautions were taken, but the results were in every case too low. The average discrepancy was, in the Kjeldahl, 0.04 per cent.; in the Gunning, 0.14 per cent. It would seem, therefore, that both of these precautions are advisable, and the second absolutely necessary, at least when working with high percentages.

Table III shows the results obtained on No. 1 by the modified Kjeldahl and Gunning methods, and by Winton's modification of the latter.

TABLE III. RESULTS ON SAMPLE NO. 1.

Calculated.	Modified Kjeldahl.	Modified Gunning.	Winton's Modification.
10.00	9.93	9.86	10.03
....	9.98	9.72	9.97
....	9.97	9.83	9.99
....	9.84	9.80	10.02
Average	9.93	9.80	10.00

The results by Winton's method are highly satisfactory; those by the Kjeldahl hardly so when compared with the other samples, while the Gunning gives results which are entirely too low to be called good.

Winton's modification of the Gunning-Kjeldahl method is essentially as follows: The substance is treated with the usual acid mixture and allowed to stand two hours, with frequent shaking. Two grams of zinc dust are then added and the first heating performed as in the Kjeldahl. Potassium sulphate is then added and the operation finished as in the Gunning method. It

<sup>1</sup>Average by both methods, see above.

is, therefore, a combination of the two with the improvement of the longer digestion in the acid mixture.

To return to the results on sample No. 1, since all the mixtures contain more or less phosphoric acid, the only substances peculiar to this sample are ammonium sulphate and potassium chloride. Since ammonium sulphate is formed in the process and is the final form of all nitrogen present, its presence in the sample could hardly account for the discrepancy, which, therefore, appears to be due to the chloride.

In looking over the record of the Association of Official Agricultural Chemists, we find that the modified Kjeldahl method has been tested by the Association in the year of its adoption and, with one exception, every year since on from one to five samples. Only four of these have contained chlorides, and only one in any considerable quantity. The modified Gunning has been tested by the Association on only one sample containing chlorides. These samples with the approximate percentages of chlorine, total nitrogen, and nitric nitrogen, and the variation in results reported, expressed in percentage of total nitrogen present, are shown in Table IV. All results which are so far from the average as to indicate accident are omitted, according to the custom followed by the reporters of the Association in averaging their results.

TABLE IV. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.  
SAMPLES CONTAINING CHLORIDES.

Sample	Method	Chlorine, per cent.	Total Nitrogen, per cent.	Nitric Nitrogen, per cent.	Variation, per cent.
No. 4, 1888	Modified Kjeldahl	5	3.16	1.64	33.4
No. 1, 1889	" "	1.5	15.91	15.91	3.0
No. 3, 1889	" "	2.5	3.55	1.48	14.1
No. 2, 1893	" "	1.5	5.77	3.47	8.8
No. 2, 1893	Modified Gunning	1.5	5.77	3.47	7.5

To further test this question, determinations were made, in duplicate, on samples Nos. 2, 3, and 4, with one-half gram of potassium chloride added. Table V shows the average results with and without chlorides, the methods being carried out in exactly the same way as before.



TABLE V. PER CENT NITROGEN FOUND WITH AND WITHOUT CHLORIDES.

No.	Calculated.	Modified Kjeldahl.		Modified Gunning.	
		Without KCl.	With KCl.	Without KCl.	With KCl.
2 .....	8.50	8.51	8.37	8.50	8.35
3 .....	8.50	8.48	8.40	8.50	8.25
4 .....	8.10	8.12	8.04	8.08	7.92
Average	8.37	8.37	8.27	8.36	8.17

A portion of the sodium nitrate used in preparing these mixtures was now taken. It had shown by the silica fusion method 16.41 per cent. nitrogen. The modified Kjeldahl showed 16.39 per cent and 16.38 per cent.

Portions of one-half gram were taken for each determination, and mixed with the same amount of potassium chloride. The digestion was carried out in the usual way.

The results were :

Modified Kjeldahl.	Modified Gunning.
16.32	15.82
16.09	15.68
15.96	15.83
15.97	15.46
16.23	16.02 <sup>1</sup>
15.95	15.99 <sup>1</sup>
16.07	15.86 <sup>1</sup>
16.13	

The Winton modification was then tried and care taken to warm gently for some time after adding zinc dust before raising the heat, which was done gradually.

Results were :

16.27
16.30
16.30
16.34
Average 16.30

Indicating that the greatest care in the reduction process will not entirely prevent loss.

To ascertain more definitely at what stage in the operation the loss occurs, mixtures of one gram each sodium nitrate and potassium chloride were treated as in an analysis, and the gases escaping from the flask were made to pass through a bulb-tube

<sup>1</sup> Two grams salicylic acid used.



containing potassium hydroxide. The nitrates and nitrites thus recovered were converted into ammonia and estimated by means of Nessler's reagent, using for comparison a solution of ammonium chloride containing 0.0001 gram nitrogen in each cc. The operation was divided into four stages: (a) addition of sulphuric salicylic acid mixture; (b) addition of reducing agent; (c) gentle heating till frothing ceased; (d) brisk boiling for a few minutes. After evolution of gas had ceased in the first and second stages, and after removal of the flame in the fourth, a glass tube was inserted through the stopper reaching nearly to the surface of the liquid, the bulb-tube attached to an aspirator, and the gases contained in the flask thus drawn through the alkali. The following table (VI) shows the results obtained, expressed in terms of per cent. nitrogen on the basis of one gram substance:

TABLE VI  
Nitrogen Recovered.

Reducing Agent used.	Temperature.	a.	b.	c.	d.	Total.	b, c, and d.
Zinc dust .....	20°	0.023	0.006	0.026	0.008	0.063	0.040
" " .....	24°	0.027	0.005	0.034	0.013	0.079	0.052
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in presence of K <sub>2</sub> SO <sub>4</sub> .....	22°	0.090	0.027	0.061	0.017	0.195	0.105
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in absence of K <sub>2</sub> SO <sub>4</sub> .....	20°	0.090	0.027	0.035	0.013	0.165	0.075
Zinc dust <sup>1</sup> .....	27°	0.039	0.001	0.006	0.011	0.057	0.018

Where zinc dust was used the acid mixture contained two grams of salicylic acid; where thiosulphate was used, one.

The results indicate: 1. That the greatest losses occur on the addition of the acid mixture and on the first application of heat. The former is thought to be due to the liberation of hydrochloric acid in direct contact with the nitrate before the mass has become thoroughly wetted by the sulphuric salicylic acid mixture.

2. The total loss exclusive of the first stage is greater with thiosulphate than with zinc dust, and appears to be greater when potassium sulphate is added with the thiosulphate than when the latter is added alone. By exercising care in the addition of the reducing agent and the application of heat, the loss in the last three stages is reduced to a very small amount.

<sup>1</sup> Some precautions taken as in working Winton's modification on mixture of nitrate and chloride, see above.

3. At a given temperature, the loss on addition of acid is greater where the mixture containing less salicylic acid is used.

4. Using the same quantity of salicylic acid, the loss on addition of the acid mixture appears to increase with the temperature.

5. The total amount of nitrogen recovered being less than the average discrepancy showed by analysis under similar conditions, it appears probable that there may be some loss later on in the process.

These facts explain why the Kjeldahl gave better results on the mixture of nitrate and chloride than did the Gunning; while the Winton gave better than either.

In this connection the heat generated on the addition of the reducing agent is of interest. The average of seven determinations each on zinc dust and thiosulphate, both added in the usual way, showed, for the former, an increase of temperature of 21°; for the latter, of 40°.

In the opinion of the writer, the prolonged digestion of the Winton method is useful, in the presence of chlorides, not only in securing complete solution of the nitrate, but also in allowing the contents of the flask to cool (for the heat generated by the action of the acid mixture on the chlorides is considerable) and to absorb a slight amount of moisture from the air, thus rendering the action less violent when zinc dust is added.

Mixtures of one-half gram each sodium nitrate and potassium chloride, treated with acid mixture cooled down to 8°, and digested as in the Winton method before addition of zinc dust, showed by the modified Kjeldahl method 16.34 per cent. and 16.32 per cent., or 99.6 per cent. of the amount found in the absence of chlorides.

Determinations by the modified Gunning on the same mixtures, in which the acid mixture was cooled to from 8° to 12°, the thiosulphate added slowly and with constant shaking and cooling of the flask, and the boiling continued some time after the liquid had become colorless, showed 16.02 per cent., 15.88 per cent., 16.16 per cent., and 15.99 per cent.; average, 16.01 per cent., or only 97.8 per cent. of the amount found when chlorides were not present.

Determinations on the same sample of pure nitrate alone by the modified Gunning method, carried out in slightly different ways, gave the following results :

As usually carried out with mixed fertilizers, 16.16 per cent. and 16.13 per cent.

Thiosulphate added first and heated before adding potassium sulphate, 16.16 per cent. and 16.24 per cent.

Thiosulphate added slowly with shaking and cooling, but digestion stopped as soon as liquid became colorless, 16.10 per cent.

Thiosulphate added as above, digestion continued one hour after colorless, 16.31 per cent. and 16.32 per cent.

As above, permanganate used, 16.37 per cent.

Modified Kjeldahl, using thiosulphate (five grams added direct), showed 16.37 per cent. and 16.36 per cent.

It may be well to state now that all the results given in this paper are corrected for reagents. At first a blank was run with every five determinations. After three or four such blanks had been made for each method and found to agree closely, their average was taken and applied to every result obtained by that method. Whenever it was necessary to change any of the reagents, another blank was run.

The results here given would *seem* to warrant the following conclusions.

1. For ordinary fertilizers containing little or no chlorides, the official methods are perfectly reliable if the directions are followed closely and the digestion in the modified Gunning is continued for at least a short time after the liquid has become practically colorless. The discrepancies which sometimes occur under these circumstances are believed to be due to faulty preparation of the sample.

2. In working with samples containing considerable amounts of chlorides, it is advisable to use the modified Kjeldahl (zinc dust) method and to cool the acid mixture before adding it to the substance. It appears advisable also to digest for some time at ordinary temperature before adding zinc dust. No way has been found by which equally accurate results can be obtained by the modified Gunning method in the presence of large amounts of chlorides, together with high percentages of nitric nitrogen.

3. When determining high percentages of nitric nitrogen by the modified Gunning method, it is necessary either to continue the boiling for some time after the contents of the flask have become colorless, or to use permanganate to complete the action.

MARYLAND AGRICULTURAL COLLEGE,  
COLLEGE PARK, MD.,  
February 20, 1895.

## ON CONDENSATION; AND ESPECIALLY ON THE CONDENSATION OF NITRIC ACID.<sup>1</sup>

BY EDWARD HART.

Received January 7, 1895.

THE ideal condenser, economically considered, is the one simplest in construction, most accessible for repairs or other purposes, and which, with a given efficiency, requires the least cooling liquid. The old-fashioned worm is certainly far removed from this ideal. The Liebig's condenser is a nearer approach. If the space between the inside and outside tube in Liebig's apparatus is made narrow enough it is possible to effect complete condensation in a relatively short tube, and to raise the cooling liquid to boiling temperature. At first sight it would seem that this gives a maximum efficiency; but it does not. If the water used as cooling liquid has, at the start, a temperature of 0°, and, as it issues from the condenser, a temperature of 100°, the heat absorbed by a given weight of water is approximately 100 units. If, however, the cooling liquid can also be made to evaporate, the heat absorbed is much larger in amount, and is equal to 100 units plus the amount required to evaporate it (526 units). This makes in all 626 units, or an efficiency six times as great. In the Liebig's condenser, also, the liquid condensed is cold or nearly so. In many cases this is not necessary and then an additional loss is sustained.

In the apparatus which I shall describe a very brief consideration will show that the maximum of efficiency may be attained. For, first, the cooling water is evaporated; second, the condensed liquid is boiling hot.

This condenser I have used in several modified forms adapted

<sup>1</sup> A paper with this title was read at the World's Congress of Chemists, Chicago, August 26, 1893. The present paper has been revised to accord with more recent experience and practice.

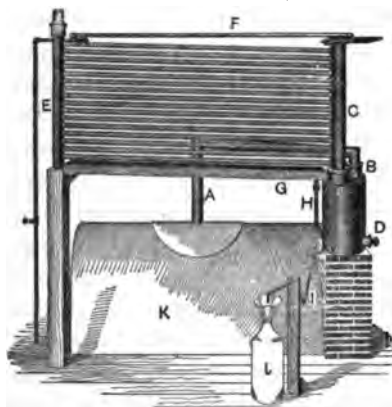
to various special purposes, among others, to the cooling of ammonia gas and the condensation of nitric acid.

In its simplest form, as used for preparing distilled water for example, the apparatus consists of a pipe with return bands placed one above the other, so that the vapor passes through the pipe in an upward direction, first right then left then right again, and so on, the bends rising one directly over another.<sup>1</sup> This pipe should be so large in diameter that the liquid may flow down in the lower part of the tube while the vapor is passing upward above it. For the same reason each bend of the pipe should have a slight rise so that the water may run down more rapidly. At the lower end the pipe should be enlarged and provided with an inverted siphon to act as a trap and carry off the condensed water. If, now, steam be passed up the pipe and water showered over the topmost bend, the water will, as it trickles down, become heated and evaporate. It is clear that by properly regulating the flow of steam and of water, we may secure complete condensation of the former and complete evaporation of the latter; at the same time the condensed water as it passes from the trap will have the boiling temperature. The cooling effect, if the apparatus is placed in the open air, is greater even than theory would predict for we have the additional cooling effect of the air. I have used this apparatus also for the separation of water vapor from ammonia gas, and for cooling the latter previous to condensing it. The conditions here are much the same as in the apparatus for distilled water. It is necessary to keep the condensed water at boiling heat to prevent reabsorption of ammonia, and in practice we find that very little ammonia is contained in this condensed water. The inclined tube acts besides as a very effective washer for the gas, completely removing any impurities mechanically carried over from the still. If it is desired to cool the condensed liquid, this is best done in a smaller apparatus of the same sort in which the current of liquid passes in an upward direction.

In the condensation of nitric acid the substances which can be used for the condenser are glass and stoneware, and it is therefore best to modify the apparatus somewhat, for the sake of sim-

<sup>1</sup> I have previously described a form of this apparatus which may be used for fractional distillation. See Am. Chem. J., 6, 178.

plicity and for decreasing the pressure in the pipes, which causes loss and annoyance by leakage through joints, and pinholes in the stoneware. With this in view the stream of vapor has been subdivided by passing it through a number of glass tubes with slight fall sufficient to allow the condensed liquid to flow back into the receiver. In the apparatus shown in the figure, the



upright tubes at either side are made of stoneware, the connecting tubes are of thin glass. The pipe A, made of stoneware, carries the nitric acid vapors from the retort into the pot B provided with a stopper, D, which is taken out if frothing should occur and allows the froth to escape without danger of filling the condenser. The vapors pass up into C and are distributed

through the glass tubes luted into it. The condensed acid runs back and is discharged through the glass trap I into the container J.

The use of the glass tube is of great advantage since the color and amount of acid can be seen throughout the distillation and the firing regulated accordingly. From the pot the vapors ascend into the stoneware pipe and pass through the nearly horizontal glass pipes let into it into another similar stoneware tube on the left, from which the chlorine and lower oxides of nitrogen escape to the chimney or tower. These tubes are slightly inclined, and the acid condensing runs back into the pot. In running back it becomes very hot by contact with the vapors coming over and is deprived of the oxides of nitrogen. Condensation is effected by running water over the glass tubes from the perforated pipe above.

This apparatus is, to a certain degree, self-regulating. It never happens that the tubes condense the gas in equal amount. One of them is thinner or a little wider, and as condensation is more rapid the flow of gas into the tube is more rapid. But, in

any event, the pressure is equal in all the tubes, and only when the distillation is hurried too much will any uncondensed vapor pass through. There are fifteen tubes to each condenser about an inch in diameter and six feet long.

Two of these condensers have been in use for nearly two years at the works of Baker and Adamson, Easton, Pa., and the system has, therefore, had a thorough test. The retorts used here are cylindrical, as shown in the cut, and are made entirely of cast iron with iron heads. The niter-cake is drawn while fluid. These retorts each hold a charge of 1,000 pounds sodium nitrate. They are charged at 7 A. M. and the operation finished at 3. P. M., a total of eight hours. The best practice by the Griesheim system is, ordinarily, a charge of eight cwt. in twenty-four hours; under favorable conditions, and with a good fireman, sixteen hours are needed.

The floor-space required in this apparatus is reduced to a minimum. The condensers are, as shown in the cut, placed over and above one side of the brick arch which covers the cylindrical retort, so that absolutely no additional floor-space is required, all that is needed being sufficient room to pass conveniently between the retorts.

One man can run several retorts. All the assistance needed is that of a helper in discharging the retorts and in emptying the salt cake from the pans. These operations will require, perhaps, half an hour each.

In another place I have already (*J. Anal. Appl. Chem.*, 5, 382) pointed out the advantages of giving a cylindrical form to the retort, which requires less floor-space, less cost for masonry, and is less expensive in coal consumption. The form I have used is very much superior to, and quite different from, any of the patterns shown by Guttman (*J. Soc. Chem. Ind.*, 12, 203). In brief, this new form of condenser has the following good points:

1. It gives great efficiency with small first cost.
2. It requires but little water.
3. It requires but little floor-space.
4. It reduces the pressure and so reduces leakage.
5. It is easily and cheaply repaired.

## SOME POINTS IN THE DISTILLATION OF NITRIC ACID.<sup>1</sup>

BY EDWARD HART.

Received January 7, 1895.

IN a previous paper I described a tube condenser for use, among other things, in the condensation of nitric acid. Further experience with this condenser has enabled us to obtain still better results. We can now obtain a distillate very low in nitrogen peroxide. The specific gravities of the distillate are about as follows:

84 pounds.	1st distillate.....	Sp. gr., 1.527
83 "	2nd " .....	" 1.526
83 "	3rd " .....	" 1.523
82 "	4th " .....	" 1.512
77 "	5th " .....	" 1.504
77 "	6th " .....	" 1.493
74 "	7th " .....	" 1.487
74 "	8th " .....	" 1.485
47 "	9th " .....	" 1.474
47 "	10th " .....	" 1.448
57 "	11th " .....	" 1.300
785 "		

The amount of fuel necessary is surprisingly low if proper care is taken. For the distillation of 1,000 pounds nitrate, we use regularly but 150 pounds of pea anthracite coal, working day turn only; this is, no doubt, largely due to the short time within which the distillation has been brought by the use of this condenser, the distillation proper occupying but six hours, and the entire time, including charging and discharging, eight hours. During the night the retort and masonry, of course, cool off. I have no doubt that by running two shifts—day and night—the coal necessary could be brought within 125 pounds for the same weight of nitrate.

*Source of the Nitrogen Peroxide Produced.*—The contrast in color between nitric acid produced on the small scale in glass, and that made on the large scale in iron retorts, is very noticeable and I have been at some pains to look into the cause, since this formation often represents a dead loss to the manufacturer. I shall later on call attention to a period in the ordinary distillation during which, with no increase in the firing, the acid

<sup>1</sup> Read at the Boston Meeting, Dec. 27, 1894.

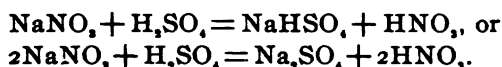


comes over very rapidly. It has often been noticed that during this stage, the acid is unusually white. I attribute this to the rapidity with which the gas passes from the retort, and consequent decrease in decomposition caused by the radiated heat. The same thing is noticed by distilling in glass. Certainly, therefore, part of the nitrogen peroxide is due to too long heating of the vapor, and the importance of an efficient condenser and a rapid distillation is evident.

The effect of concentration of the vitriol on the color is very evident. The ease with which concentrated nitric acid is decomposed is well-known and, as might be expected, the strong acid made from distilled vitriol and dry nitrate shows much stronger color than that made from the less concentrated materials. In glass, heating over a Bunsen, such acid may be obtained without difficulty of only a pale straw color, but in the ordinary iron retort the crude aqua fortis will frequently contain as much as three per cent. nitrogen peroxide.

It is the common opinion among acid makers that part of this color, perhaps a large part, is due to action of the acid on the iron. In most cases this is no doubt true, as the retort, as ordinarily set, is but imperfectly heated at the ends. In the retorts which I have been using, however, the retorts are *entirely* surrounded with the fire gases. It is quite possible, however, that even here the iron is notably attacked. Part of the color, no doubt, arises from impurity of the materials—chlorine, organic material, and iron in solution principally—but I suspect that this is responsible for only a part of the trouble. A gentleman who has for years carried on the distillation of nitric acid on the large scale, recently informed me that he had distilled fused nitrate and white vitriol in iron with no perceptible diminution of the color in the product.

As stated in the books, the only reactions occurring are



In practice only the first reaction is usually employed, especially where, as in acid for mixed acids, to be used for nitroglycerol, the product must be as concentrated as possible. In this

connection, however, one point I think should be noted that seems to have escaped attention, that is, that with weak vitriol the water is largely retained by the cake until the last stage of the operation, and greatly assists the decomposition giving a fair acid and a cake which is practically infusible. If, however, strong vitriol is used, the decomposition is incomplete and the acid exceedingly red.

*The Frothing.*—This matter of frothing is one that frequently gives great trouble to the nitric acid distiller, especially where weak acid and wet nitrate are used. The frothing begins in such cases after about seven-elevenths of the acid has distilled over.

This is easily demonstrated by conducting a distillation in glass with acid of 1.80 sp. gr., or less. The trouble becomes then plainly apparent, and is evidently due to the decomposition of the  $\text{NaHSO}_4$  at first produced into  $\text{Na}_2\text{S}_2\text{O}_3$  and water:  $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ . That this is the reason may easily be demonstrated by heating in another similar retort a mixture of dry sodium sulphate and sulphuric acid. We then have  $\text{NaHSO}_4$  formed, and on continuing the heat the same frothing is noticed, although the distillate is, of course, entirely free from nitric acid. Frothing over is prevented by giving sufficient capacity to the retort, and by care and skill in firing. Neither alone is sufficient to prevent it.

*Rate of Distillation.*—One of the most remarkable things in the distillation, especially noticeable in glass and with pure dry materials, is the variation in the rate of distillation and the almost explosive evolution of acid, which takes place, for a short period, after about three-tenths of the acid has distilled over. For example: In distilling in glass 200 grams sodium nitrate and 235 grams distilled sulphuric acid, the proportions required by the equation  $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$ , the following results were obtained. It should be understood that the Bunsen, over which the operation was conducted, was allowed to remain untouched, except where noted, and that the apparatus was shielded from air currents. The thermometer bulb was shielded from radiation by placing it within a porcelain crucible in the retort.

Time.	Time interval.	Temperature.	Temperature interval.	Acid distilled.	Remarks.
1:46:40	.....	108°	...	..	Distillation begun.
2:48:23	1:43	110°	2°	5	
2:50:20	1:57	113°	3°	10	
2:52:30	2:10	117°	4°	15	
2:55:15	2:45	124°	7°	20	
2:59:00	3:50	128°	4°	25	
3:02:00	3:00	133°	5°	30	Froth rises.
3:02:55	0:55	125°	-8°	35	Froth very high.
3:03:30	0:35	125°	0°	40	Froth sinking.
3:04:00	0:30	125°	0°	45	No froth
3:04:45	0:45	126°	1°	50	No froth.
3:17:40	12:55	135°	9°	55	{ Mushy mass fusing to clear liquid below.
3:23:30	5:40	148°	13°	60	Half fused.
3:38:30	.....	157°	9°	65	Three-fourths fused.
3:45:20	.....	152°	-5°	70	{ Piece of cake dropped into fused mass, lowering temperature.
3:52:00	.....	158°	{ Acid not running, clear fusion, lamp turned up.		
3:58:30	.....	170°	12°	75	No froth.
4:03:00	.....	178°	8°	80	No froth.
4:04:45	.....	180°	Lamp turned still higher.		
4:06:00	.....	194°	14°	85	Slight froth.
4:08:15	.....	200°	6°	90	Half-inch froth.
4:12:20	.....	220°	20°	20	{ Retort full of froth during this interval.
4:16:00	.....	246°	26	96	{ Froth gone, lamp turned out.

The drop of the temperature at 133° is, I think, unmistakable, and reminds one of the rise of temperature produced in the crystallization of a supersaturated solution. There we have the change from the fluid to the solid condition—here from the solid to the fluid. This explosive evolution is noticeable also in distilling in iron on the large scale and, perhaps, explains in part the difficulty nitric acid makers have hitherto had in properly condensing their product. By proper firing, and with a properly set retort, this difficulty is lessened.

To decompose strong nitric acid by heat or by its action on iron, and then to drive off the nitrogen peroxide with great pains and loss, is evidently a clumsy and probably unnecessary operation. I shall, therefore, make a determined effort to so arrange the retort that this will be in future unnecessary. There would seem to be no insuperable obstacle in the way of so conducting the distillation that even the first distillate would be of a pale straw color, like that made in glass, and quite fit for the manufacture of dynamite and other nitro compounds with no purification whatever.

The use of nitro compounds has, of late years, become so large that a rational method of conducting the process of nitric acid distillation is imperatively called for.

Berthelot has shown that strong nitric acid is completely decomposed at about  $360^{\circ}$  into nitrogen peroxide, oxygen, and water. It is certain that with the retorts entirely surrounded by fire gases the temperature of the upper part of the retort exceeds  $100^{\circ}$ . It is not surprising, therefore, that the first distillate should show a dark red color. A recent distillation in glass, with pieces of cast iron immersed in the mixture of acid and nitrate, gave no additional color to the first distillate.

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### NEW BOOKS.

COD-LIVER OIL AND CHEMISTRY. BY F. PECKEL MÖLLER, PH.D. London: Peter Möller. New York: Wm. H. Schieffelin & Co. Printed for private distribution.

This book is really two books in one. The first part treats of cod-liver oil, the methods of catching the fish, the preparation of the oil, and an account of its constituents. We learn that cod-liver oil was originally made from fresh cod-livers by the steam process, by Peter Möller, in 1853. The oil so prepared was a great improvement over the older product prepared by the putrefaction of the livers. It still, however, caused disagreeable after-effects when exhibited, and to remedy this an investigation was undertaken by P. M. Hyerdahl, presumably in the employ of Peter Möller. Mr. Hyerdahl finds that the disagreeable after-effects are caused by the presence of hydroxy acids in the oil, and that these may be excluded by rendering the livers in an atmosphere of carbon dioxide. This process is now carried out by Peter Möller, therefore buy your cod-liver oil of this firm. The deduction is not so stated in the book, which is well written and gives a very readable account of the subject, but the advertising purpose is obvious.

It is a pity that Mr. Hyerdahl's work was not made known through the regular channels—the *Berichte* for example. Chemists will be apt to look with suspicion upon statements so obviously interested.

The second part of the book is a treatise on organic chemistry of an original sort. The author has used the Daltonian symbols in modified form, and the result is, as might have been expected, that the poor devil of a printer has had a hard time of it. So long as printing is done as at present, authors should beware of using new characters; by so doing they not only increase the already difficult task of the printer but really put themselves at his mercy. If only one printer have the character he must be allowed to do the printing of course. While such symbols have certain advantages, their disadvantages seem greater. Only a few people seem to be able to remember that, after all, our symbols represent only very imperfect knowledge, and that they are only tentative. A chemist can, therefore, read this treatise with interest and profit; it can scarcely be considered a good book for beginners, but it was probably not intended for beginners.

EDWARD HART.

THE INCREASE IN WEIGHT OF TIN AND LEAD ON CALCINATION. BY JEAN REY, 1630. Alembic Club Reprints, No. 11. 54 pp. Edinburgh: William F. Clay, 1894.

Rey is one of the less well-known investigators of the seventeenth century. He is properly to be classed with Hooke, Mayow, and Boyle, or the Oxford School of Chemists, as Thorpe has fitly called them, in their work upon the increase of weight of the metals when calcined, and the part played by the air in these processes. That which Thorpe has so well done for the others is now done for Rey in this little book. The quaintness of the original is well preserved in the translation, and the book is very valuable as giving an insight into the wisdom and the childishness of the times. His self-applause in the triumphant summing up of the evidence in support of his theory, that the air played an important part in the phenomena observed, is delicious.

The Alembic Club is doing a most valuable work for the science in the republication of these early essays. They are interesting and helpful to the earnest student and should have a wide circulation.

F. P. VENABLE.

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## OBITUARY.

### PROFESSOR MARK POWERS.

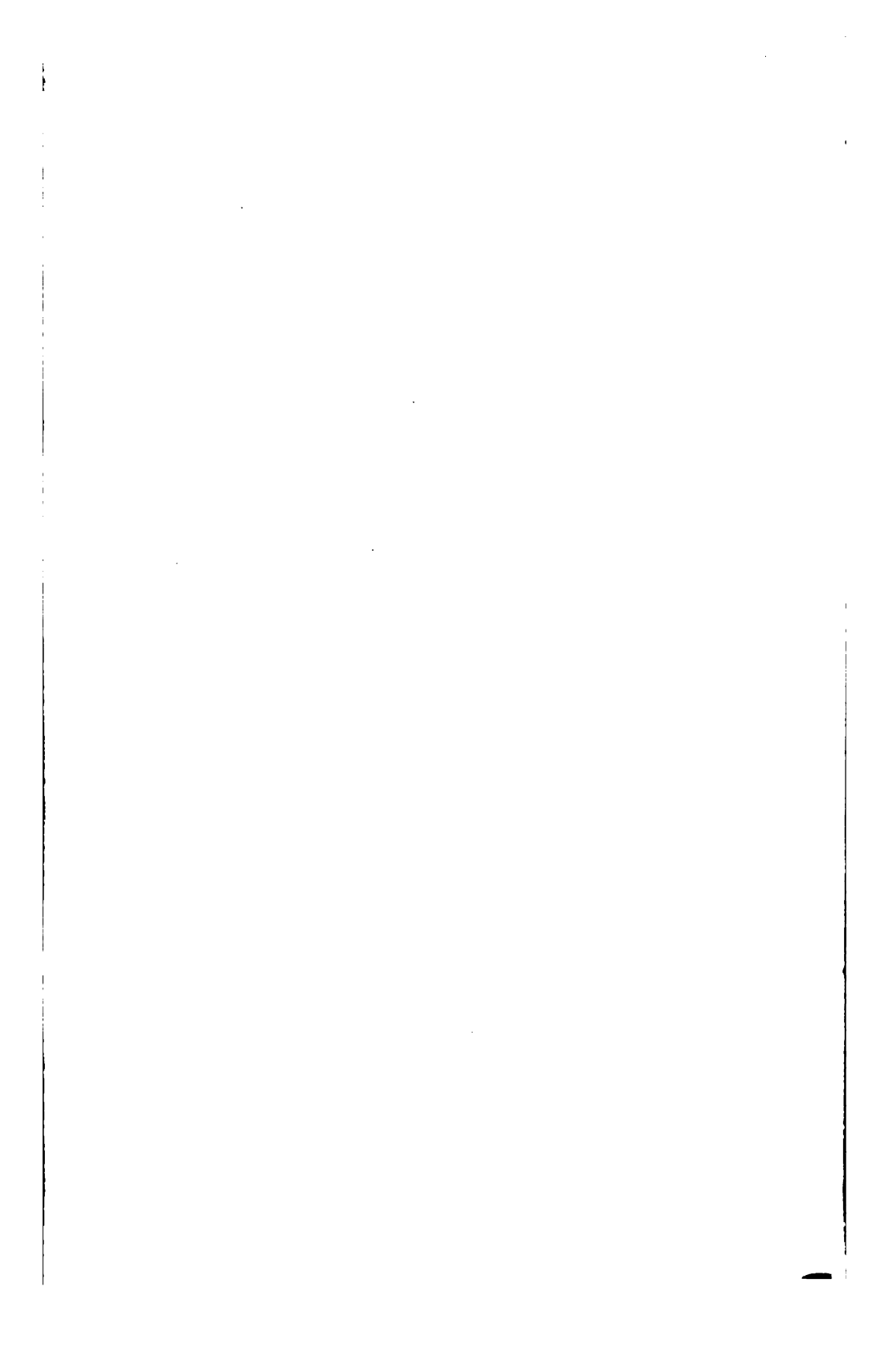
Professor Mark Powers, a member of the American Chemical Society, died in Chicago, March 1st, of smallpox.

Professor Powers was born near Muncie, Ind., November 13th, 1864. In September, 1883, he entered the Freshman class of the University of Illinois, where, in time, he gave special attention to chemistry, then in charge of Professor Wm. McMurtrie. He was graduated from the University, with the highest honors of his class, in June, 1887. In September of the same year he came to Chicago to take the position of Assistant in the Chemical Laboratory of the School of Pharmacy of the Northwestern University. At the time of his death he was Assistant Professor of Chemistry in the same institution.

Professor Powers possessed unusual ability as an analyst and investigator, yet, on account of his many duties in the laboratories, he was able to publish only one scientific paper. This was a valuable contribution on "The Decomposition of Organic Matter in Water," and is found in the *Journal of Analytical Chemistry*, Vol. III. As a teacher his work was of the highest order, and it was in this direction, rather than in that of investigation, that he chose to make a reputation.

J. H. LONG.

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*Arthur E. Moore*



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE CHEMICAL NATURE OF DIASTASE.<sup>1</sup>

BY THOMAS B. OSBORNE.

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FEW substances are of more importance or of more interest than the enzymes or unorganized ferments, yet our knowledge relating to these bodies is almost wholly confined to the products of their activity and the conditions under which this is manifested. Although the existence of these ferments was recognized early in the present century, our information in respect to their true nature is exceedingly limited and unsatisfactory. It was for a long time supposed that the active substance causing a fermentative change is a soluble proteid, and the power of inducing such change seems by many to have been ascribed to soluble proteid matter in general. Later, this power was thought to be restricted to special forms of proteid, but no sufficient evidence was brought forward. Of late years investigators have undertaken to isolate ferments and prepare them in a state of purity. The results of these attempts have led to very conflicting conclusions respecting the character of these bodies. Some of the so-called pure preparations of ferments have had the properties of the proteids, and have more or less agreed with them in composition, while others have differed widely from the proteids in both respects.

It still seems to be the opinion of many that the enzymes are ....

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in fact true proteids and that the ferments thus far supposed to be obtained in a state of purity were simply somewhat contaminated with other substances. This opinion is based on the fact that all those changes which are ascribed to the action of enzymes occur only in solutions which contain proteid matter, and that the activity of the ferment is greatly influenced by conditions known to have a pronounced action on proteids, such as heat, the presence of acids and alkalies, salts of the heavy metals, etc.

The first discovered and one of the most carefully studied of these ferments is diastase. The practical application of the action of diastase in the manufacture of alcohol and of malt liquors has given rise to careful and extended studies of the conditions affecting the activity of this ferment, and the result of these studies has led some to the opinion that the active substance is the albumin present in the malt extracts. The conversion of starch into maltose and dextrin by diastase increases in rate and extent as the temperature of the solution is raised, until the heat reaches the point at which the albumin begins to coagulate. The ferment then begins to lose power, and, when the heat is sufficient to completely coagulate the albumin, its amylolytic action ceases entirely. In 1883, C. Lintner, Jr., showed that the diastatic power of fifteen different samples of malt was very nearly proportional to the amount of coagulable albumin which they contained. In 1886, however, C. J. Lintner prepared diastase in, as he supposed, a state of purity, and came to the conclusion that the results of his analysis of diastase indicate that, in the ferments, we have a special class of proteid substances. The composition of Lintner's purest diastase differed much from that of the proteids, since it contained only two-thirds as much nitrogen and also less carbon. His diastase furthermore, failed to give the reaction with cupric sulphate and potassium hydroxide which is characteristic of proteid matter. These results of Lintner's threw much doubt on the hypothesis that the vegetable albumin is identical with diastase.

In my investigations of the proteids of wheat, rye, and barley, I found in all these grains the same albumin and was impressed with the close relation between the temperature at which this albumin coagulates and the temperature at which diastase begins

to lose its activity. The aqueous extracts of these seeds, as is well known, possess considerable diastatic power, and it seemed to be more than probable that this was due to the albumin. I accordingly undertook an investigation of this subject, and I now offer the results thus far obtained, which are preliminary to a more extended study.

The usual method of preparing vegetable enzymes is to treat the aqueous or glycerol extract containing them with alcohol as long as a precipitate, having fermentative power appears, to purify this by repeated precipitation from its solution in water, by means of alcohol, and finally to subject the aqueous solution to dialysis to remove salts. This method is wholly unsuited to yield pure preparations, because the precipitate produced by alcohol contains not only a large amount of carbohydrates and salts, but also nearly all of the various forms of proteid matter present in the extract. Lintner employed this method, and there can be no doubt that he obtained a mixture of proteids with other substances which defied all attempts at further separation.

The most rational method (hitherto very little used) is first to separate the proteids from the carbohydrates and other soluble substances by saturating the extract with ammonium sulphate, thereby precipitating the ferment and proteids together, next to remove the proteid existing as globulin, by dialysis, and then, if possible, to separate the albumin and proteoses by fractional precipitation with alcohol. In following this method, a measured quantity of malt extract was saturated with ammonium sulphate, the precipitated proteid matter was filtered out, dissolved in water, and the clear filtered solution made up to the volume of the original extract. This solution was found to have the same diastatic power as before precipitation, thus showing that ammonium sulphate had not injured the diastase. Throughout my work diastatic power has been measured by Lintner's method, which gives a very ready means of accurately comparing different preparations. This method consists in adding to each of a series of carefully measured volumes of the solution containing definite amounts of the diastatic preparation, ten cc. of a two per cent. solution of soluble potato starch, and allowing the ferment

to act upon the starch for one hour at the ordinary temperature of the room. At the end of this time five cc. of Fehling's solution are added to each portion and the mixtures are heated for ten minutes in a boiling water-bath. After the precipitated cuprous oxide has settled, where too little sugar has been formed to precipitate all the copper, the liquids will be blue; if sugar is in excess they will be yellow. The one colorless liquid that should result gives the measure of diastatic power. Lintner represented the value of his most active preparation by 100, and that of the other preparations by figures stating the amount of each necessary to give a complete reaction with Fehling's solution under the above conditions, in comparison with his most active preparation, of which, under the conditions of the test just described, twelve one-hundredths of a milligram completely reduced the five cc. of Fehling's solution.

For the sake of comparison I have measured the activity of my preparations by the same standard, so that a preparation whose activity is given as 200 means that six one-hundredths of a milligram sufficed to give a complete reduction.

As Lintner recommended extracting the malt with water containing twenty per cent. of alcohol instead of pure water, since thereby less foreign matter was removed with the proteid, this procedure was first tried. Fifteen hundred grams of ground air-dried malt, prepared in the laboratory, were treated with three liters of twenty per cent. alcohol, the extract squeezed out in a press, and the residue again treated with another liter of the same dilute alcohol. Three liters of extract were obtained which, after being filtered clear, were saturated with ammonium sulphate. Owing to the presence of the alcohol much less ammonium sulphate was dissolved than by a water extract, and the proteids were consequently incompletely precipitated. The precipitate obtained was treated with water and a considerable quantity of insoluble matter, consisting mostly of globulin, rendered insoluble by contact with the reagents, was filtered out. The solution was saturated with ammonium sulphate, and the precipitate dissolved in water. This clear solution was then dialyzed in water for some days, and after filtering from a slight deposit was dialyzed in alcohol of 0.845 sp. gr. for forty-eight hours.

As the water passed out of the dialyzer faster than the alcohol entered, the solution became concentrated and a considerable precipitate formed. This was filtered out and washed, first with dilute alcohol and afterwards with absolute alcohol, and dried over sulphuric acid. This preparation, I, when thus dried, dissolved in water with the exception of a not inconsiderable residue. When filtered clear, the solution, on heating, gave an abundant coagulum, and after boiling and filtering out the coagulum, the filtrate gave a strong pink color with cupric sulphate and potassium hydroxide, showing the presence of proteose. The diastatic power of this preparation, in comparison with Lintner's best was eighty-six, but, as it was afterward found to contain a comparatively small amount of ash, the test was repeated with the addition of a few milligrams of sodium chloride and then found to equal 150.

The composition of preparation I was as follows:

PREPARATION I.		Ash-free.
Carbon .....		52.55
Hydrogen .....		6.48
Nitrogen .....		16.41
Sulphur } .....		24.56
Oxygen }		
		<hr/> 100.00
Ash.....		2.29

These figures indicate that this preparation consisted almost wholly of proteid matter, and the reactions proved the presence of at least three forms; namely, coagulated proteid, albumin, and proteose. This mixture was one and a half times more active than Lintner's most energetic preparation, and contained about six per cent. more nitrogen and one-half as much ash. The composition of the preparation is very similar to that of the coagulated albumin-like body obtained from wheat, rye, and barley, and for which I have adopted the name leucosin. As this albumin has been found to have the same composition, whether coagulated by heat or by alcohol, and as most, if not all of the proteids have identical composition (so far as analysis can show), in the soluble and the coagulated states, it seems probable that

preparation 1 consisted mostly of coagulated and soluble leucosin together with a little proteose.

The filtrate from this preparation on addition of absolute alcohol, yielded a small precipitate, 2, which dissolved wholly in water and gave only a very slight coagulum on heating, but a strong pink biuret reaction, showing it to be mostly proteose. Its diastatic power was only nineteen.

As above stated, owing to the presence of alcohol, saturation of the original extract of malt with ammonium sulphate, precipitated only a part of the proteids. Accordingly the filtrate from this first precipitation was dialyzed for twenty-four hours, so as to remove most of the alcohol, and was again saturated with ammonium sulphate. The resulting precipitate was dissolved in water, filtered from a slight residue, and the clear solution dialyzed until nearly all the ammonium sulphate was removed. The dialyzer was then transferred to alcohol and left for forty-eight hours. The resulting precipitate was then filtered out and treated in the manner before described. After drying, this substance, preparation 3, like preparation 1, consisted of insoluble proteid, soluble leucosin, and proteose. Its diastatic power was 133, and it had the following composition:

#### PREPARATION 3.

	Ash-free.		Average.
	I.	II.	
Carbon.....	52.34	....	52.34
Hydrogen.....	6.73	....	6.73
Nitrogen.....	15.90	15.92	15.91
Sulphur } .....	....	....	25.02
Oxygen } .....	....	....	100.00
Ash .....			0.82

The filtrate from this preparation was next treated with a large quantity of absolute alcohol, and the contained proteid completely thrown down. This substance, preparation 4, dissolved entirely in water; its solution yielded but a trace of coagulum on heating, and when boiled and filtered gave a strong proteose reaction. It contained, ash-free, only 12.02 per cent. of nitrogen, and had a diastatic activity of 11.

These results prove that extraction of the malt with twenty per cent. alcohol is not suited for a subsequent precipitation of the proteids with ammonium sulphate; that otherwise the method is capable of yielding preparations of diastase of high fermentative power, which to a certain extent can be separated into fractions containing the different forms of proteid matter; that the fractions including the greatest amount of soluble albumin have the greatest diastatic power; and that a part at least of the proteose is almost, if not entirely, free from this power.

Another extraction was made on a much larger scale, so that the fractional precipitations might be more numerous, and the fractions examined more closely.

Ten kgms. of malt were exhausted with water and the extract was saturated with pure and neutral ammonium sulphate. The very bulky precipitate was suspended in four liters of water and dialyzed until much of the sulphate had been removed and the precipitated proteid largely dissolved. The solution was then filtered from an insoluble residue consisting mostly of globulin, and the clear filtrate was saturated with ammonium sulphate. The precipitate thus obtained was suspended in 1500 cc. of water and was dialyzed until nearly all the sulphate had been removed and the precipitate mostly dissolved. The globulin contained in the extract was thus largely separated and, after it had been filtered out, the clear solution was dialyzed into an equal volume of alcohol of 0.84 sp. gr. After forty-eight hours the precipitate, number I, which had separated, was filtered out and set aside for further examination. The filtrate was again dialyzed into an equal volume of alcohol of 0.84 sp. gr., and after forty-eight hours another precipitate, II, obtained. The filtrate was further dialyzed into a rather large quantity of somewhat stronger alcohol, and precipitate III separated, and by similarly treating the filtrate from this, precipitate IV was obtained, the filtrate from which, on adding a large quantity of absolute alcohol, yielded precipitate V. All the proteid in the extract was thus separated. Precipitate I was much contaminated with coloring-matter, II less so, and III was nearly colorless, as were also IV and V.

The approximate weights of each of these precipitates was as

follows: I, thirteen grams; II, eight; III, six; IV, five; and V, three, a total of thirty-five grams.

Precipitate I was treated with water and found to be very largely insoluble. The insoluble matter was filtered out and washed with water, and the clear solution was dialyzed for several days to remove all the salts. No proteid was thus precipitated, and the dialysis was continued in strong alcohol, thereby throwing down all but a trace of proteid. The precipitate, preparation 5, weighed 2.11 grams. After drying, it dissolved in water with the exception of a small residue, and its solution when slowly heated became turbid at 65° and deposited flocks at 70°. After boiling and filtering out the slight coagulum, the solution gave a strong pink reaction with the biuret test. These tests show the preparation to consist largely of proteose. Its composition was as follows:

PREPARATION 5.

	Ash-free.
Carbon .....	53.16
Hydrogen .....	7.03
Nitrogen .....	16.50
Sulphur.....	1.50
Oxygen .....	21.81
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	100.00
Ash .....	0.49

With Lintner's test this preparation showed a diastatic power of thirty.

The insoluble residue, remaining after treating precipitate I with water, was thoroughly extracted with ten per cent. sodium chloride solution; what remained insoluble in this menstruum was filtered out and the clear solution dialyzed until free from chlorides. The precipitate thus formed, preparation 6, weighed one and two-tenths grams, and after drying was not soluble in water, but dissolved readily and nearly completely in salt solution, having, as was to be expected, the properties of a globulin. This substance had a very slight diastatic power, and its sodium chloride solution when heated slowly became turbid at 60°, a few flocks appearing at 65°, due to a trace of albumin. Its composition was as follows:



## PREPARATION 6.

	Ash-free.
Carbon .....	53.11
Hydrogen .....	6.45
Nitrogen .....	15.78
Sulphur } .....	24.66
Oxygen } .....	
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	100.00
Ash .....	0.75

The filtrate from preparation 6 still contained proteid matter which was separated by dialysis in alcohol. Preparation 7 was so obtained, weighing 1.54 grams, having the same properties as 6, and the following similar composition :

## PREPARATION 7.

	Ash-free.
Carbon .....	53.58
Hydrogen .....	6.70
Nitrogen .....	15.87
Sulphur } .....	23.85
Oxygen } .....	
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	100.00
Ash .....	1.43

After extracting precipitate I with water and salt solution a very considerable part still remained undissolved. This was treated with water to remove all the salt, and then with alcohol, and was dried over sulphuric acid. This preparation, 8, weighed eight grams and was quite dark in color. It had the properties of an insoluble form of globulin, being dissolved in one-half per cent. sodium carbonate solution and precipitated therefrom by neutralization. Its composition was nearly the same as that of the two last globulin-like preparations and is probably a so-called "albuminate" derived from that substance. The composition of preparation 8 was :

## PREPARATION 8.

	Ash-free.
Carbon .....	53.55
Hydrogen .....	7.01
Nitrogen .....	15.72
Sulphur .....	1.23
Oxygen .....	22.49
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	100.00
Ash .....	1.09

Precipitate II was treated with water and the solution thus

formed was dialyzed in water for several days and then in alcohol for twenty-four hours. A quantity of absolute alcohol was finally added to the contents of the dialyzer, thus completely precipitating the proteid. This preparation, after drying, was almost wholly soluble in water, and when heated slowly its solution became turbid at 60° and deposited flocks at 66°. The amount of proteid thus coagulated was somewhat greater than was given by preparation 5, and its diastatic power was likewise greater, being seventy-five. Analysis showed its composition to be as follows :

## PREPARATION 9.

	Ash-free.
Carbon.....	53.19
Hydrogen.....	6.71
Nitrogen.....	16.74
Sulphur.....	1.38
Oxygen.....	21.98
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	100.00
Ash.....	0.78

This preparation contained a slight amount of insoluble matter, some albumin and much proteose.

The residue of precipitate II, which was not dissolved by water, was treated with sodium chloride solution and the clear extract dialyzed till free from chlorides, but as no precipitate was produced, the dialyzer was transferred to alcohol when preparation 10 separated, weighing 0.49 gram, and containing, ash-free, 15.18 per cent. of nitrogen. It is probable that this is the same globulin obtained in larger quantity from precipitate I, but less pure. That part of precipitate II which remained undissolved after extracting with water and salt solution, was then washed thoroughly with water and with alcohol, yielding preparation 11, which weighed 5 grams and had the following composition :

## PREPARATION 11.

	Ash-free
Carbon.....	53.51
Hydrogen.....	6.75
Nitrogen.....	15.76
Sulphur.....	1.12
Oxygen.....	22.86
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	100.00
Ash.....	0.66

These figures show that precipitate II contained less globulin and proportionately more leucosin and proteose than precipitate I and it was accordingly found to be more powerfully diastatic.

Precipitate III was in turn treated with water, the resulting extract filtered clear, dialyzed for several days in water, and then in alcohol, absolute alcohol being finally added in quantity to the contents of the dialyzer. The resulting precipitate, preparation 12, weighed three grams. It was almost completely soluble in water, and its solution when slowly heated became turbid at 55° and flocculent at 60°. The amount of this coagulum was much greater than that yielded by preparation 9. The filtrate from the coagulum gave a strong proteose reaction. The diastatic power was 222, indicating the presence of much more diastase than any of the preceding preparations. Its composition was as follows:

## PREPARATION 12.

	Ash-free.
Carbon .....	52.80
Hydrogen .....	6.96
Nitrogen .....	16.09
Sulphur .....	1.45
Oxygen .....	22.70
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	100.00
Ash .....	0.59

The residue of precipitate III was digested with salt solution, the filtered extract was dialyzed in water till free from chlorides, and then, as no proteids separated, the dialysis was continued in alcohol. Only 0.28 gram of proteid resulted, which, without correction for ash, contained 12.53 per cent. of nitrogen. This was marked preparation 13, and considered to be impure globulin.

The part of precipitate III still undissolved was washed with water and with alcohol, yielding preparation 14, which weighed 2.87 grams. This had the following composition:

## PREPARATION 14.

	Ash-free.
Carbon .....	53.25
Hydrogen .....	7.65
Nitrogen .....	16.12
Sulphur .....	1.38
Oxygen .....	21.60
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	100.00
Ash .....	0.55

This preparation has a somewhat higher nitrogen and lower carbon content than preparations 8 and 11, which is probably due to its being a mixture of the insoluble form of the globulin with some insoluble albumin coagulated by the long contact with alcohol to which it had been subjected. This is to be expected, as precipitate III contained relatively more albumin than precipitates I and II.

Precipitate IV was next treated with water, the solution filtered clear, dialyzed for some days in water, and afterwards transferred to alcohol, and the dialysis continued. Absolute alcohol was then added to the contents of the dialyzer, giving preparation 15, weighing four grams. This substance dissolved in water to a nearly clear solution, which, when filtered perfectly clear and heated carefully, became turbid at 50° and gave a large coagulum at 56°. After heating the solution and filtering off the coagulum, a good reaction for proteose was obtained with the biuret test. This preparation had a diastatic power of 600. As this was a much more powerful ferment than any yet produced, its properties were carefully studied and will be described at length later. When analyzed this substance was found to have the following composition :

## PREPARATION 15.

	Ash-free.
Carbon .....	52.50
Hydrogen .....	6.72
Nitrogen .....	16.10
Sulphur .....	1.90
Oxygen .....	22.78
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	100.00
Ash .....	0.66

It will be noticed that the sulphur in this preparation is a little higher than in the preceding preparations, which is probably due to its containing some sulphate.

The part of precipitate IV which did not dissolve in water was treated with salt solution, but no globulin was extracted. The residue was then washed with water, giving preparation 16, which weighed 0.9 gram and had the following composition :

## PREPARATION 16.

	Ash-free.
Carbon .....	53.42
Hydrogen .....	7.15
Nitrogen .....	16.65
Sulphur } .....	22.78
Oxygen } .....	
	100.00
Ash .....	0.24

The composition of this insoluble product shows it to be probably coagulated leucosin.

A portion of precipitate V, when treated with water, was found to dissolve completely. It was therefore washed with absolute alcohol, yielding preparation 27, which weighed 2.87 grams. The clear solution of this substance when heated became turbid at 50°, and yielded a small coagulum at 58°. Boiled and filtered, a strong pink coloration was given with the biuret test, thus showing it to consist mostly of proteose. The diastatic power of this substance was 60, only one-tenth that of preparation 15. Its composition was:

## PREPARATION 17.

	Ash-free.
Carbon .....	51.21
Hydrogen .....	6.52
Nitrogen .....	15.40
Sulphur } .....	26.87
Oxygen } .....	
	100.00
Ash .....	2.37

The lower nitrogen content of this preparation indicates that the strong alcohol had thrown down, together with the proteids, some non-nitrogenous substances.

Much is to be learned by studying these results which will be of service in future attempts to isolate pure diastase.

In the first place, it is plain that we have in our malt extract a globulin, an albumin, and at least one, more probably two, forms of proteose. I believe the substance soluble in salt solution to be a true globulin, since it so readily assumes an insoluble form, and also because a much larger quantity of the same

body was obtained by extracting with ten per cent. salt solution, the malt residue remaining after the extraction with water. I also think that at least two forms of proteose are present, for the water-soluble portion of precipitate I consisted chiefly of proteose, as did also precipitate V. The amount of proteose diminished from precipitate I to precipitate IV, which contained the least, while precipitate V, which, it will be remembered, was thrown down by adding to the solution a very large amount of absolute alcohol was mainly proteose. A part of the proteose was precipitated by alcohol more readily than the albumin, while another part was less readily precipitated. Beside the albumin, globulin, and proteose, we have also to take account of the "albuminate" or insoluble forms of the albumin and globulin. The results of this extraction show that the globulin is rendered insoluble more rapidly than the albumin, so that precipitation with alcohol and solution in water, repeated a few times, may be depended upon to remove the former. Whether repeated fractional precipitation can be employed to completely separate the albumin from the proteoses is not so certain. The albumin is thrown down from the malt extract by saturation with magnesium sulphate, and it is not unlikely that a complete separation can be accomplished by this reagent. It is, however, not to be forgotten that the diastase may be a substance which, when heated to from 50°-60°, splits apart into an albumin and a proteose, and that the proteose found in the solutions which have been heated is a decomposition product of the diastase. Kühne's attempts to produce pure trypsin led him to suspect that this ferment is a body which, when heated, yields a coagulable fraction and a proteose-like substance. Hammarsten's more recent work on a nucleoproteid obtained from the pancreas also points strongly in this direction.

Now that we have some precise knowledge of the associated substances, it seems probable that we may succeed in obtaining diastase nearly, if not quite, pure, and arrive at a clearer and more positive knowledge of this ferment, and also have a guide in further study of other enzymes, which will lead to a more satisfactory understanding of this whole subject. It is probable that the ferments contained in seeds are much easier to prepare than

those of animal origin, since the substances with which they are associated are largely non-proteid and comparatively easy to separate. It is also certain that the amylolytic ferments present an easier problem than the proteolytic, for the products of the activity of the latter are so similar, in their nature, to that which the ferment is supposed to possess, as to make it always a matter of great uncertainty whether the separated enzyme is free from those bodies or not.

As already stated, preparation 15 was a very energetic ferment, and on this account its properties were more fully studied, with the following results:

Dissolved in water this substance gave all the usual proteid reactions, and when heated slowly became turbid at  $50^{\circ}$  and gave a flocculent coagulum at  $56^{\circ}$ . This is exactly the temperature of coagulation of the albuminum (leucosin) which I have prepared from wheat, rye, barley, and malt, with identical composition and properties. The aqueous extracts of these grains have, moreover, a strong diastatic action on starch. The amount of coagulable albumin in preparation 15 was determined and found to be 53.2 per cent. of the dry substance.

These facts point strongly to the albumin as being the diastatic substance, yet there are several facts hard to explain, if this be true, which cannot be overlooked. Although in general the diastatic power of my preparations was greater the larger the amount of coagulable albumin they contained, I have never yet been able to establish any numerical relations between the two. In no case have I found any diastatic action with solutions free from albumin. Furthermore, the activity of my preparation 15 is such as to require a much greater diastatic power for malt than this shows if its coagulable albumin is the enzyme.

A malt extract corresponding to a solution of the diastase in five milligrams of malt had the same diastatic power as 0.02 milligram of preparation 15. As the preparation contained but a little over fifty per cent. of coagulable albumin, this would correspond to only 0.01 milligram of albumin in the five milligrams of malt, or two-tenths per cent. The amount of albumin in malt is much greater than this, as it is also in wheat, rye, and barley, whose diastatic power is greatly inferior to that of malt. It is

not probable that the *separated* diastase is more active than that *in the seed*, especially in view of the experiments which follow, comparing the action of malt extract and preparation 15. The only explanation of this that occurs to me, is that the active diastase is a combination of albumin with some other body, presumably the proteose, which breaks up on heating, yielding coagulated albumin, and that, besides this combined albumin, free albumin is also present, which has no diastatic power, but which is coagulated at the same time. There is no direct evidence, however, that this hypothesis is correct.

Compared with other so-called pure ferments, preparation 15 is very active. At 20° it was in a condition to produce, from soluble starch, over 2000 times its weight of maltose and a further undetermined quantity of dextrin, within one hour. After having been dried over sulphuric acid and kept for six months, its activity was reduced to one-half, but in this condition it produced in seventeen hours, at 20°, 10,000 times its weight of maltose besides an unknown quantity of dextrin. At 45° the same quantity of maltose was produced in one hour as at 20°. At 50° much less and at 55° very little maltose was formed. These tests were made by using an amount of diastase solution just sufficient to produce enough maltose at 20° to exactly reduce five cc. of Fehling's solution.

Compared with malt extract of the same diastatic strength, as measured by the amount of maltose produced in one hour at 20°, the distilled water solutions of preparation 15 have a less powerful action in liquefying starch paste. Five cc. of malt extract added to ten cc. of a starch paste containing two per cent. of starch, dissolved the starch completely in eight minutes, while the solution of preparation 15 required thirty-seven minutes.

The malt extract is also more energetic in converting starch completely into bodies giving no color with iodine. Five cc. of the same malt extract added to ten cc. of soluble starch solution caused the blue reaction with iodine to disappear in thirteen minutes, while it required thirty-eight minutes to reach the same result with the solution of the separated diastase. When, however, the diastase was dissolved in malt extract, whose enzymes



had been previously killed by heating, the difference between the separated diastase and that in the malt extract nearly disappeared.

Two test-tubes were each charged with ten cc. of starch paste. To one tube were added five cc. of fresh malt extract, and to the other the same amount of boiled and cooled malt extract in which had been dissolved a quantity of preparation 15, sufficient to make a solution of the same sugar-producing power as the fresh malt extract itself.

The fresh malt extract liquefied the starch in seven minutes, the mixture of preparation 15 and boiled malt-extract in fourteen minutes, while thirty-seven minutes were required to produce the same result with a distilled water solution of preparation 15. In completely converting starch into bodies giving no color with iodine, the solution of preparation 15 in boiled malt extract gave exactly the same result as the fresh malt extract, showing that the difference first noticed was due to the conditions and not to the ferment.

In view of these results, it seems highly probable that diastase is a true proteid, for if we consider the extremely minute quantity of preparation 15 required to produce large amounts of maltose, it is hard to believe that this action is due to some substance adhering to the proteid to the extent of only three or four per cent. at the most. If such were the case it is also remarkable that the enzyme should adhere in so much greater quantity to the particular precipitate represented by preparation 15 than to any of the other numerous fractions. If diastase, then, is to be considered as a true proteid, it is evidently either an albumin, a combination of an albumin with a proteose, or a proteose. We have seen that those fractional precipitates which consist largely or wholly of proteose have little or no diastatic action, amylolytic power being manifested most strongly in the fractions containing the most albumin, and least in those containing but little, though not in strict proportion to the amount of the albumin. It is to be concluded that the diastatic enzyme is most closely related to the albumin, named leucosin, and it is not improbable that further careful study will show more clearly what this relation is.

## NOTE ON THE PURIFICATION OF GLUCINUM SALTS.<sup>1</sup>

BY EDWARD HART.

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**T**WENTY years ago I found glucinum in a clay brought to Dr. Drown's private laboratory, in Philadelphia, for analysis. The experience gained then in making the separation from alumina showed clearly that none of the methods then known gave a satisfactory separation. In dissolving the carbonate we found that alumina also dissolves, and that in treating the oxides with solution of ammonium chloride, alumina as well as glucina dissolves.

In beginning the purification of glucina from beryl, which I have undertaken for a more careful study of the metal and its alloys, I determined, if possible, to prepare it in some other way than by the use of the time-honored ammonium carbonate method which, besides giving a material of doubtful purity, is expensive and tedious. Such a method has been found based on the properties of the mixed sulphates from beryl, and which seems not to have been used for this purpose. Perhaps it will be best to describe the method now used in full, without describing the failures through which the work passed.

The powdered beryl is first fused with mixed carbonates and then ground and washed with water. The powdered mass is then mixed with sulphuric acid and evaporated to make the silica insoluble. The sulphate solution obtained from this material is evaporated and treated with an excess of potassium sulphate. Alum crystallizes out and is purified by recrystallization. The mother-liquor contains the glucinum along with the iron and alkaline sulphates. Potassium chlorate is added in excess, and the solution heated to peroxidize the iron. Sodium carbonate solution is now added, little by little, the solution being boiled after each addition until a filtered sample shows no yellow color. The whole solution is then filtered, and the glucinum which will be contained in the filtrate is precipitated by further addition of sodium carbonate.

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

The method, of course, depends upon the fact that it is impossible to throw down the glucinum until the greater part of the acid has been saturated, the glucinum remaining in solution as basic sulphate. Iron and aluminum, on the contrary, are easily separated. Some care is needed in order to get rid of the last trace of iron, which persistently remains in solution until the point at which the precipitation of glucinum begins is almost reached.

A sample prepared in this way was perfectly soluble in hydrochloric acid, gave no reaction for iron with potassium ferrocyanide, was completely soluble in an excess of ammonium carbonate and caustic potash. The ammonium carbonate solution gave no precipitate on the addition of ammonium oxalate. The method is exceedingly simple, convenient and cheap, and leaves nothing to be desired.

## THE COMPOSITION OF THE TUBERCULOSIS AND GLANDERS BACILLI.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received April 30, 1895.

WHILE many examinations of the products of bacilli have been made during the past years comparatively little attention has been paid to a comparison of the proximate and ultimate analyses of the germs themselves that are morphologically different, and produce different pathological changes.

Cramer<sup>1</sup> gives the results and analyses of cholera germs from different sources, and concludes that upon easily assimilable media the composition of the bodies of the same germ from different sources, and which vary in virulence, is about the same. Where, however, the media supply food that is but difficultly assimilable the composition of the bodies of the germs will vary. The comparison which he makes between these and several other species shows a variation which indicates a distinct and characteristic composition for each germ.

We have had occasion to collect large quantities of the tuberculosis and glanders bacilli, and have submitted the germs, grown both on the ordinary glycerol beef broth and on artificial

<sup>1</sup> *Arch. f. Hygiene*, 16.

media, to proximate and ultimate analyses. The results are presented in tabulated form.

The germs were freed by filtration from the culture liquid and the last traces of the soluble products removed by washing either with water alone or with the addition of sodium carbonate. The germs were then dried over sulphuric acid and, just before analysis, were further dried at  $100^{\circ}\text{C}$ . In drying, the germs underwent but slight change of color if they had been thoroughly washed. The analyses were made with the germs obtained from one and the same original culture, but the growths of eight or ten different generations were mixed together to secure an average sample. The artificial media used for the cultivation of the tuberculosis bacillus had the following composition:

Water.....	1,000 cc.
Glycerol.....	70 grams.
Acid potassium phosphate.....	1 gram.
Ammonium phosphate.....	10 grams.
Sodium chloride.....	10 "
Asparagin.....	2 "
Magnesium sulphate.....	0.2 gram.

In table I are given the determinations of the carbon, hydrogen, nitrogen, phosphorus, sulphur, ash, in column I, calculated upon the weight of the sample dried at  $100^{\circ}\text{C}$ .; in column II, upon the ash free substance. With the exception of the nitrogen there seems to be but little variation in the composition of the germs grown on beef broth or on artificial culture media.

I. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS TUBERCULOSIS.

	Beef broth.		Beef broth.		Beef broth.		Artificial media.	
	Per cent.		Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.	I.	II.
Carbon.....	....	....	60.12	62.61	62.98	64.06	62.16	63.35
Hydrogen.....	9.22	9.60	9.15	9.53	7.39	7.52	9.19	9.36
Nitrogen.....	7.34	7.64	7.27	7.40	8.04	8.18	8.94	9.14
Sulphur.....	0.44	0.45	....	....	....	....	0.22	0.23
Phosphorus soluble in dilute nitric acid... }	0.66	....	0.19	....	....	....	....	....
Phosphorus, total (Carius).. }	0.77	....	0.83	....	0.87	....	0.66	....
Ash.....	4.03	....	4.03	....	1.77	....	1.92	....

Table II gives the elementary analyses of the bacillus of glanders. The germs for these analyses were filtered off, washed a number of times with water and cold absolute alcohol and dried.

A comparison of these results with those of the bacillus of tuberculosis shows a great and distinctive variation.

II. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS MALLEI.

	Beef broth.	
	Per cent.	
	I.	II.
Carbon .....	41.81	44.89
Hydrogen .....	5.89	6.20
Nitrogen .....	14.05	14.81
Sulphur .....	0.99	1.04
Phosphorus, total (Carius).....	1.10	....
Ash .....	5.18	....

The variations in the composition of these two bacilli is still more apparent in a comparison of the amount of the proximate constituents as shown in tables III, IV, V, and VI. The determinations were made according to the general methods prescribed for such analyses. The nitrogen determinations were made by the Kjeldahl method, and from these results the albuminoids were calculated. The figures reported in the table as cellulose were obtained by treating the residue from the alcohol extract with 1.25 per cent. caustic soda for forty to sixty minutes, washing well, then digesting the residue with 1.25 per cent. sulphuric acid for the same length of time, washing, and drying. The loss by ignition of the dried residue should indicate cellulose.

The presence of cellulose in the organs of tuberculous individuals has been examined by Freund, Dreyfuss, Toyosaku Nishimura, with somewhat discordant results. Freund (*Jahr. d. g. Wiener Aerzte*, 28, 1886) treated the organs and blood from twenty-five different cases, first by extracting with ether and alcohol, then with dilute sulphuric acid. In this way there were left behind hard round lumps about the size of tubercles, which, while insoluble in dilute were soluble in strong sulphuric acid. This solution diluted with water and heated gave the reduction test for sugar.

III. *BACILLUS TUBERCULOSIS. Beef Broth 1.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	39.64	41.29	38.95	40.32	39.29	40.80
Alcohol extract .....	.....	.....	.....	.....	.....	.....
Albuminoids.....	45.81	47.31	45.87	47.85	45.84	47.53
Cellulose .....	6.95	7.24	.....	.....	6.95	7.24
Ash.....	4.12	.....	3.94	.....	4.03	.....

IV. *BACILLUS TUBERCULOSIS. Beef Broth 2.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract .....	.....	.....	.....	.....	.....	.....
Alcohol extract .....	3.04	3.10	.....	.....	3.04	3.10
Albuminoids.....	50.25	51.12	45.43	46.25	47.84	48.68
Cellulose .....	7.37	7.68	.....	.....	7.37	7.68
Ash.....	1.67	.....	1.87	.....	1.77	.....

V. *BACILLUS TUBERCULOSIS. Artificial Media.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	37.76	37.88	37.98	38.71	37.57	38.34
Alcohol extract .....	4.69	4.79	4.19	4.28	4.44	4.53
Albuminoids.....	55.87	57.12	.....	.....	55.87	57.12
Cellulose .....	3.82	3.89	5.69	5.80	4.75	4.84
Ash.....	1.92	.....	.....	.....	1.92	.....

VI. *BACILLUS MALLEI. Beef Broth.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	7.91	8.26	7.67	8.09	7.78	8.17
Alcohol extract.....	.....	.....	.....	.....	.....	.....
Albuminoids.....	89.81	94.68	85.71	90.43	87.76	92.55
Cellulose .....	5.87	6.19	.....	.....	5.87	6.19
Ash.....	5.18	.....	.....	.....	5.18	.....

Schulze's method was also used. Lungs, spleen, peritoneum, and dried blood were cut up finely and subjected to the action of nitric acid and potassium chlorate, white, round nodules, or a flocculent substance were left behind, which, submitted to analysis, after solution in cupric ammonia and reprecipitation, gave results corresponding to cellulose.

Nishimura<sup>1</sup> used for experiment the lungs and blood of tuberculous cows and also of men. The organs, after being finely divided were extracted with ether and alcohol and then with two per cent. sulphuric acid.

The residue, when treated with strong sulphuric acid, gave a solution that yielded the Trommer sugar test only twice out of six experiments.

Nishimura then tried the alkali method. The material was fused with potassium hydrate in the oil-bath at 180° C., the fusion acidified with sulphuric acid, then made slightly alkaline and allowed to stand until clear. The residue was filtered off and tested for cellulose. By this method, from the lungs of a grown person a slight reaction for cellulose resulted with Trommer's test. The spleen and liver, treated in the same way also indicated cellulose. In two cases from children, lungs, liver, and spleen gave the cellulose test.

How should this cellulose content be present in the organs? The most plausible supposition is the assumption that this comes from the presence of the bacilli themselves, and that the bodies of the latter are rich in cellulose. Upon this assumption Dreyfuss<sup>2</sup> examined several varieties of bacilli, *bacillus subtilis*, *pus bacillus*, *aspergillus glaucus*, and by the fusion method with caustic potash, succeeded in obtaining the reduction and phenylhydrazine tests.

Nishimura, found, however, that other bacilli, *e. g.*, the water bacillus No. 28, did not show the presence of cellulose. He extended his researches to the tubercle bacilli themselves. He made four tests upon the tubercle bacilli from glycerol bouillon cultures, using the alkali method, but obtained no reduction. From this he concludes that cellulose is not present in the tubercle bacilli.

In our examination of the tubercle bacilli, as indicated above, the digestion of the residue, after extraction with ten per cent. sulphuric acid gave distinct reduction tests with Fehling's solution. In two experiments Hoppe-Seyler's method, by fusing with caustic potash at 180°, was used. In the one a good reduction test was obtained; in the other the reduction test failed.

<sup>1</sup> *Arch. f. Hygiene*, 21, [1], 52.

<sup>2</sup> *Ztschr. Physiol. Chem.*, 18, [3, 4], 367.

From these tests we would conclude that cellulose is present in the tubercle bacilli, but in very minute amount, which may, in some instances, escape detection by the methods generally adopted. Nishimura thinks that possibly the tubercle bacilli form cellulose when they grow in the body, but not on artificial culture media. The fact, however, that the analyses indicated cellulose, both when grown upon glycerol beef broth and upon the mineral salt cultures, would make it probable that the cellulose is a normal constituent and can be produced by the germ from whatever material it feeds upon.

The proximate analyses of the glanders bacilli show results which are markedly different from those obtained with the tubercle bacilli. While the determination of cellulose by the method of difference would indicate its presence, the fusion with caustic potash, according to the same method adopted for the tubercle germs, and subsequent treatment with sulphuric acid indicates the absence of cellulose. Care was taken in filtering the tuberculosis and glandery germs that they were not contaminated with cellulose from filter-paper. The most of them were filtered through porcelain and then scraped off.

In order to show more clearly the variation in the body composition of different germs the following table is appended which gives results obtained by Cramer and others, with different germs, upon varying media. The change in the nitrogen content is very marked, and while the difference of medium influences this to some extent there is still sufficient variation in the different germs to permit of a possible distinction of species. While the products of germs are invaluable as an aid to identification it would appear that the chemical study of the bodies of the germs and the differences in their proximate constituents, especially albuminoids and fat, and a more distinctive study of the albuminoids might be very useful in aiding classification.

In order to form some idea of the composition of the fat extracted from the tuberculosis and glanders bacilli, the fats were saponified with caustic soda and the fatty acid separated. The quantity of acids obtained, however, was small and it was only possible to make melting-point determinations. From these the acids of the glanders seemed to be oleic and palmitic, those from the tubercle bacilli, palmitic and arachidic acid.



The difference in the fatty acids apparent in these two, and which would probably vary as much in other germs, could doubtless be made of use in classification. This study is being continued further and extended to the hog cholera, swine plague, and allied germs.

Media	Albuminoids per cent.			Ether and alco- hol extract per cent.		Ash per cent.	
	1 per cent Peptone agar.	2 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Peptone agar.
	1 per cent Peptone agar.	2 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Peptone agar.
<b>Bacilli.</b>							
Pfeiffer's capsule bacillus .....	66.6	70.0	....	14.06	....	9.10	....
Pneumonia bacil- lus .....	71.7	79.8	....	11.3	....	10.36	....
Bacillus of Rhi- noscleroma ....	68.42	76.2	....	9.1	....	9.33	....
Spirillum of chol- era .....	....	64.96	....	....	....	...	30.78
No. 28.....	73.1	79.6	....	17.08	....	7.79	....
<b>Nitrogen.</b>							
	7 per cent Glycerol beef broth. per cent	7 per cent Artifi- cial media. per cent	5 per cent Glycerol beef broth. per cent	1 per cent Peptone beef broth. per cent	Car- bon. per cent	Hydro- gen. per cent	Ash. per cent
	7 per cent Glycerol beef broth. per cent	7 per cent Artifi- cial media. per cent	5 per cent Glycerol beef broth. per cent	1 per cent Peptone beef broth. per cent	Car- bon. per cent	Hydro- gen. per cent	Ash. per cent
Tuberculosis ....	7.34	8.94	....	....	62.98	7.34	1.77
Glanders ....	....	....	14.05	....	41.89	5.89	5.18
Swine plague ...	....	....	....	11.81	44.57	7.20	12.41

BIOCHEMIC LABORATORY,  
BUREAU OF ANIMAL INDUSTRY.

## A CONVENIENT FORM OF UNIVERSAL HAND-CLAMP.<sup>1</sup>

BY PETER T. AUSTEN AND W. A. HORTON.

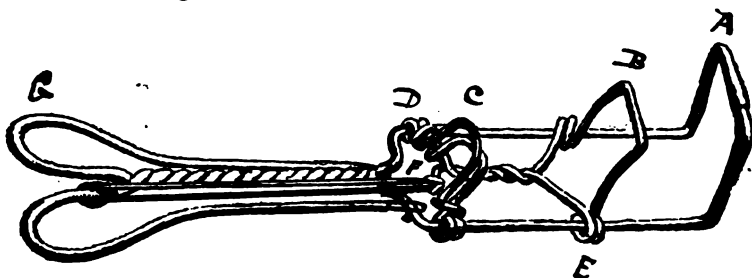
Received April 23, 1895.

THE various holders and hand-clamps used for holding test-tubes and smaller forms belong, as a rule, to two classes. The bite is effected either by a spring or by a pressure exerted by the hand. The difficulty with the first class of holders is that the spring is often inconveniently strong for delicate tubes, and not strong enough for flasks. The second class often fails when long continued holding is involved, as muscular pressure relaxes after a time.

The following little device was worked out to afford a con-

<sup>1</sup> Read before the New York Section, December, 1893.

venient holder that should take from nothing up to a diameter of an inch and a half and yet allow a grasp which corresponds to the weight of the object held, and also not tire the hand, no matter how long it is held.



The clutch B slides on the parallel bars E, and is slightly smaller than the counter-clutch A. This, with its curvature, allows it to grasp any object, no matter how small, that is placed between B and A. A double bearing, to insure ease of movement, is effected by winding the wire at D. The double arch C allows the thumb to press easily and comfortably against it, and act as a knee-joint. The swell G keeps the handle in the grasp, and the rubber strap F brings the traveling clutch back and opens the clamp as soon as the pressure is removed from C.

To use the apparatus, the handle is securely grasped and the end of the thumb is placed against C. On straightening the thumb, in the manner of a knee-joint, the object is tightly held between the clutches. The hand does not tire on continued holding because the pressure is taken in a straight line on the bones of the thumb, and hence calls for so slight a muscular action as to be practically inappreciable.

The clamp is manufactured by Richards and Company.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. I.]

### ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received April 22, 1895.

COMMUNICATIONS relating to the electrolytic separation of metals, present in solution as double cyanides, have appeared, from time to time, in this Journal and in other pub-

lications devoted to chemistry, during the past seven years. Thus it was found that in solutions, such as that mentioned, it was possible to separate *cadmium* from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium. No difficulties were encountered in these separations. About the only objection that could be presented against them, and one that would in any manner postpone their immediate adoption into general analysis, was the fact that from twelve to fourteen hours were required for the deposition of the cadmium, mercury, gold, and silver.

Not more than a year ago Smith and Spencer (This Journal, 16, 420) observed that the deposition of both mercury and silver was markedly accelerated when the electrolyte undergoing decomposition was heated from 65° to 70° C. It will be recalled that all the earlier separations noted above had been carried out at the ordinary temperature. It appeared, therefore, desirable to further extend the study, and in the lines which follow results are given which were obtained from this new point of view.

While cadmium can be completely separated from its double cyanide solution *in the cold*, the reverse occurs if the liquid be raised to 65°. Thus, in the communication of Smith and Spencer, evidence is given that in a warm solution silver can be fully separated from cadmium, and in the table below it will be observed that mercury and cadmium can be similarly separated. It was, therefore, impossible to review the separations of cadmium from the various metals from which it had been fully separated in the cold. The experiments were accordingly limited to mercury, gold, and silver with several typical metals, as the conditions under which their separation proved successful would doubtless serve for the remaining representatives of the various groups from which separations had been effected.

In the earlier communications it was customary to report the strength of the acting current in cubic centimeters of electrolytic gas per minute. In the present presentation the *normal density* (N. D.) of the current for 100 square centimeters of electrode

surface will be given in ampere units. The reader will also bear in mind that the temperature of the solutions operated upon was, in all cases, 65° C.

## MERCURY SEPARATIONS.

Mercury taken. Grams.	Mercury found. Grams.	N. D. of current in ampere units per minute.	Time required for precipitation.	Potassium cyanide in grams.	Cadmium present in grams. per cent.	Zinc present in grams. per cent.	Nickel present in grams. per cent.	Cobalt present in grams. per cent.
0.1901	0.1907	0.02	3 hours.	2	100	100	100	100
.....	0.1903	0.02	3 "	2	100	...	...	...
.....	0.1902	0.06	3½ "	2	...	100	...	...
.....	0.1900	0.06	3½ "	2	...	100	...	...
.....	0.1896	0.06	3½ "	2	...	100	...	...
.....	0.1905	0.08	3½ "	3	...	...	100	...
.....	0.1908	0.08	3½ "	3	...	...	100	...
.....	0.1898	0.08	3½ "	2	...	...	...	100
.....	0.1896	0.08	3½ "	2	...	...	...	100

In ordinary gravimetric analysis it would not be possible for the analyst to separate mercury from any one of the metals just given as completely nor as quickly as indicated in the table.

Gold was separated from cobalt, arsenic, copper, zinc, and nickel, the quantity of gold present in each trial being 0.1087 gram, and each of the other metals in equal amount. But one separation was made with each metal. The quantity of cyanide ranged from one to two grams; the period required for the precipitation of the gold varied from three to three and one-half hours. In all the trials, excepting that with copper, the current was  $N. D._{100} = 0.1$  ampere. In the exceptional case it was reduced to 0.07 ampere. The quantities of gold obtained were:

1.....	0.1084 gram.
2.....	0.1080 "
3.....	0.1093 "
4.....	0.1088 "
5.....	0.1082 "

The separations of silver were limited to zinc, nickel, and cobalt. The quantity of silver was 0.1465 gram and the other metals in equal amount. The quantity of cyanide in all instances was two grams, while the current strength was  $N. D._{100} = 0.04$  ampere. The time of deposition did not exceed three hours. The precipitated silver equaled:

1.....	0.1464 gram.
2.....	0.1464 "
3.....	0.1460 "
4.....	0.1464 "

The separation of silver from copper and from cadmium is just as rapid and complete as these last separations.

The deposits of mercury, gold, and silver, were carefully examined in the quantitative way for the various metals with which they had been associated; in every instance they showed themselves perfectly pure, so that these methods can be relied upon and trusted where accurate and rapid work is required.

The metallic deposits were washed and dried in the manner described in previous articles.

During the progress of the preceding experiments behaviors were observed pointing toward the separation of silver from gold, and mercury from gold and from silver in cyanide solution, but thus far expectations in these directions have not been realized. When conditions apparently favorable were obtained, traces of one or the other metal would be discovered in the metallic deposit, so that, at this moment, trustworthy and definite data cannot be given.

UNIVERSITY OF PENNSYLVANIA.

## ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINEBARGER.

Received May 3, 1895.

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#### I. INTRODUCTORY.

THE investigation of the elastic forces or tensions of vapors emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years. The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions. The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapor-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said, has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses. Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapor-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapor-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed

makes only a special application. It must, indeed, be allowed that the consideration of a mixture of vapors, instead of a single one, introduces certain complications into the problem; and this is, perhaps, just the reason so little work has been done on this part of the subject; still difficulties of this sort are probably not unsurmountable.

The limitations of work on vapor-tensions to dilute or, at most, moderately concentrated solutions cannot be said to be satisfactory. True, the theory of solutions has been developed on the hypothesis that dissolved matter, in analogy with gaseous matter, is in a state of considerable dilution; and experimental confirmations of theoretical predictions can be expected only when such a state of affairs is realized. Notwithstanding that circumstance, it seems of importance to extend our line of operations and attack the problems presented by concentrated solutions; perhaps they will be found to exhibit fewer anomalies than has been supposed.

There are two circumstances which render work that has hitherto been done on the vapor-tensions of mixtures of volatile liquids of all concentrations unsatisfactory; they are to be found in the choice of the liquids investigated, and the kinds of vapor-tension measured. The liquids chosen were almost invariably those which are now recognized to be made up of associated molecules; they are just those which exhibit the greatest abnormalities in respect to most of their properties, and it cannot be expected that simple relations, if they exist at all, will be discovered when such liquids are used as material of investigation. All investigators also, almost without exception, have measured only the total pressure of the mixtures of liquids examined, which is the sum of the partial pressures, these, however, being entirely unknown. But more important is it to know the share which each vapor has in the exerting of the total pressure, and only when this is learned can our knowledge of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject of vapor-tensions. The method employed is such as to permit of the specification of the partial pressures of a mixture's components, and also of their concentrations in the gaseous phase. The

choice of the liquids has been made with an eye towards employing those which have been found to be most "normal," so that in the examination of more complex liquids, that is, those consisting of associated molecules, the simplicity to be expected in the phenomena of the former may aid us in getting some light on the possible intricacies of the latter. All the mixtures examined are freely soluble in one another so that no disturbing influence from layer-formation can take place.

In reality, we have before us a case of equilibrium; the equilibrating system consists of two substances, each present in two phases, the liquid and gaseous. We have to ascertain at the points of equilibrium the temperature, the partial pressures of the two substances in gaseous phase, and their concentration in both liquid and gaseous phase.

## 2. HISTORICAL.

The first paper that I know of which treats of the vapor-tensions of mixtures of liquids soluble in every proportion in one another is by Gustav Magnus,<sup>1</sup> who states that, when to a volatile liquid, such as ether, contained in a barometric vacuum, another less volatile liquid, such as alcohol, be added, the tension of the vapors of both liquids is less than that of the ether alone; the cause of this behavior Magnus seeks in a certain reciprocal attraction on the part of the two liquids. Magnus' paper, being almost the first on the subject, contains, as, indeed, is generally the case with pioneer papers, some important statements, which, through the labors of later investigators, have become generalized into wide-reaching laws; but everything in it is purely of a qualitative nature, no reliable quantitative data being given.

Regnault<sup>2</sup> in the course of his extended investigations on the elastic forces of the vapors given off by liquids, determined at

<sup>1</sup> Ueber das Sieden von Gemengen zweier Flüssigkeiten und ueber das Stossen solcher Gemenge. *Ann. der Phys. u. Chem. Pogg.*, 38, 481-492. 1836.

<sup>2</sup> Ueber die Elasticitätskräfte der Dämpfe bei verschiedenen Temperaturen im Vacuo und in Gasen; und ueber die Spannung der Dämpfe aus gemengten oder geschichteten Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, 93, 537-579, 1854, and *Mémoires de l'Académie des Sciences*, 26, 1862. Quatrième Partie: Forces Élastiques des Vapeurs qui sont Émises par les Liquids volatiles, Melangées par Dissolution reciproque ou superposés. Troisième Classes: Mélanges binaires des Liquides qui se dissolvent mutuellement en toutes Proportions, 724 and 743.



different temperatures by the static as well as dynamic method, the vapor-tensions of several mixtures of various liquids. Regnault did not pay much attention to the composition and analysis of the mixtures investigated, his object being merely to get a general idea of the relations of the vapor-tensions of the mixtures to those of the component liquids. Still there is but a little doubt that the composition of the mixtures is specified with sufficient accuracy to admit of his data being regarded as reliable enough for theoretical considerations and confirmations. In a later section are given his results so rearranged as to furnish some indications of the nature of the phenomenon which they represent. Regnault states in the papers printed in the *Mémoires de l'Académie* that his experiments lead to the same conclusions as those of Magnus; but in the German translation (*loc. cit.*) from the *Comptes rendus*, he does not seem to have given Magnus this credit, which induced the latter in a paper<sup>1</sup> immediately following that by Regnault, to call attention to his results published some eighteen years before<sup>2</sup> (*loc. cit.*). In this last paper by Magnus nothing new is communicated, a considerable part of it being occupied with quotations from his former paper.

Plücker<sup>3</sup> determined by means of Geissler's "Vaporimeter" the composition of the liquid and gaseous phases, as well as the total pressure of the latter, of a system consisting of a mixture of alcohol and water; the work has the stamp of having been done with great care, and the accuracy of the results—rather meager, it must be said—can probably be relied upon.

Bussy and Buignet<sup>4</sup> in the course of their researches on the physical properties of mixtures of hydrocyanic acid and water, made determinations according to the static method of the vapor-tensions of seven mixtures of the above two liquids (page 245 of their memoir). The work, which was carried out at 13.25° is fairly accurate, but the range of concentrations is not extensive enough to permit of utilization of their results.

<sup>1</sup> Ueber die Spannkraft der Dämpfe von Mischungen zweier Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, 93, 579-582, 1852.

<sup>2</sup> Untersuchungen über Dämpfe und Dämpfgemenge; *Ann. der Phys. u. Chem. Pogg.*, 98, 193-220, 1854: A continuation of this article was promised by the author, but I have been unable to find it and regard its appearance as very doubtful.

<sup>3</sup> Recherches sur l'acide cyanhydrique: *Ann. Chim. Phys.*, [4] 3, 231-263, 1864.

While the preceding scientists for the most part endeavored to find relations between the tensions of vapors emitted by a mixture, and those given off by its components in a state of purity, Duclaux<sup>1</sup> set himself about to get a knowledge of the relations of the composition of the liquid mixture to that of the vapors emitted. His method consisted in distilling a large quantity (1100 cc.) of a mixture of known composition and collecting several distillates, the composition of which was determined through their surface tensions by means of the "Drop-method." Duclaux, believing, for reasons which he does not state, that simpler relations are to be discovered, if the proportions of the liquids in a mixture be expressed in volumes rather than in weights, communicates results and data, which, as he neglects to give any accurate indications as to the temperature at which and the pressure under which the mixtures investigated by him entered into ebullition, and as to the amount and direction of the change of temperature as the boiling proceeded, it is impossible to put into a shape permitting of comparison with others; the mixtures studied consisted of water and the series of alcohols up to caprylic alcohol, and of water with formic, acetic, and butyric acids.

Wüllner<sup>2</sup> determined according to the static method<sup>3</sup> the vapor-tension of five different mixtures of ethyl alcohol and water at temperature intervals of about 10° from 11.8° to 84.6°; also of two mixtures of sulphuric ether and alcohol at temperature intervals of about 3° from 7.2° to a little over 30°. Wüllner had especially in mind in his work the determination of the variation of constancy of the ratio of the tension of the mixture of vapors to the sums of the tensions of each vapor alone with the temperature; no mention is made of experimental details and of the purity of the liquids experimented upon.

It may be well for the sake of completeness to make mention

<sup>1</sup> Sur les Forces Élastiques Émises par les Mélanges de deux Liquides: *Ann. Chim. Phys.*, [5] 14, 305-345, 1878.

<sup>2</sup> "Ueber die Spannkraft der Dämpfe von Flüssigkeitsgemischen": *Ann. der Phys. u. Chem. Pogg.*, 129, 353-366. 1866.

<sup>3</sup> *Ann. der Phys. u. Chem. Pogg.*, 103, 534-542.

here of Alluard's,<sup>1</sup> Berthelot's,<sup>2</sup> and Brown's<sup>3</sup> work on the boiling points of mixtures of liquids, although little is to be found therein which bears directly upon our subject.

An important experimental as well as theoretical investigation on the subject in question has been made by Konowalow.<sup>4</sup> The method employed was the static, so arranged, however, that the error arising from the change of composition of a liquid mixture due to the evaporation of its components was reduced to a minimum. The determinations were made with mixtures of water with each of the first four members of the series of alcohols,  $C_nH_{m+2}O$ , and of the series of acids  $C_nH_{m+2}O_2$ , at several different temperatures; the work of Konowalow may be looked upon as very accurate.

Among Raoult's numerous and important publications on the vapor-tensions of solutions, there is one which deserves mention in the history of the vapor-tensions of mixtures of volatile liquids, even if one component of the binary mixtures investigated by him has but a feeble tension of vapor. The paper referred to<sup>5</sup> treats of the vapor-tensions of solutions of turpentine, nitrobenzene, aniline, methyl salicylate, and ethyl benzoate, all almost non-volatile liquids, in ether; the determinations were made at ordinary temperatures by the static method, and are to be considered as remarkably exact. In a later section, the data will be given in a modified form.

In the last five or six years papers by Planck, by LeChatelier, and by Nernst, treating of the theoretical side of the question, have appeared; from their importance as well as for convenience of reference, their contents will be quite fully reproduced.

Max Planck<sup>6</sup> enunciated certain relations between the differ-

<sup>1</sup> "Experiences sur la Temperature d' Ebullition de quelques Mélanges binaires de Liquides que se dissolvent mutuellement en tous Proportions." : *Ann. Chim. Phys.*, [4] 1, 384-392, 1894.

<sup>2</sup> "Sur la Distillation des Liquides Mélanges." *Compt. rend.*, 57, 430 (1863); *Ann. Chim. Phys.*, [4] 1, 384-392, 1864.

<sup>3</sup> "On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride" : *Transactions of the Chemical Society of London*, 39, 304, 1881.

<sup>4</sup> "Ueber die Dampfspannungen der Flüssigkeitgemischen." : *Ann. der Phys. Wied.*, 14, 219, 1881.

<sup>5</sup> "Ueber die Dampfdrucke Atherischer Lösungen." : *Ztschr. phys. Chem.*, 2, 353-373, 1888.

<sup>6</sup> "Ueber die Dampfspannung von verdünnten Lösungen flüchtiger Stoffe." : *Ztschr. phys. Chem.*, 2, 405-414, 1888.

ence of concentrations of mixtures of two volatile substances in equilibrating gaseous and liquid phases, and the depression of the vapor-tension, which permit of experimental verification. Planck assumes the applicability of the law of Raoult-van't Hoff and that of Henry to the case of the vapor-tensions of mixtures of volatile substances (liquids); that is, there must be direct proportionality between lowering of vapor-tension and molecular concentration, and also between concentration in liquid phase and partial pressure in gaseous phase; furthermore he states expressly that his deductions are made for the case of dilute solutions only, and that the substances in all phases of a system consist of normal molecules.

Such a system made up of a liquid and gaseous mixture in contact may be represented by the symbol:

$$nm, n, m, + n'm', n_1'm_1',$$

where  $n$  and  $n_1$  represent numbers of molecules, and  $m$  and  $m_1$  molecular masses; the accented letters refer to the vapor, and the unaccented to the liquid; those written with the subscript have reference to the dissolved substance, those without subscript to the solvent;  $n$  and  $n'$  are large in comparison with  $n_1$  and  $n_1'$ . The numerical concentrations of the individual substances are:

$$c = \frac{n}{n+n_1}; c_1 = \frac{n_1}{n+n_1}; c' = \frac{n'}{n'+n_1'}; c_1' = \frac{n_1'}{n'+n_1'}.$$

If a reaction supervenes occasioning the following changes in the numbers of the molecules:

$$\delta n : \delta n_1 : \delta n' : \delta n_1' = \gamma : \gamma_1 : \gamma' : \gamma_1',$$

equilibrium occurs, in case this condition,

$$\gamma \log c + \gamma_1 \log c_1 + \gamma' \log c' + \gamma_1' \log c_1' = \log K,$$

is fulfilled<sup>1</sup>;  $K$  is a function of pressure and temperature. In the case before us, we have two different reactions to consider: the vaporization of the solvent and that of the dissolved substance. Accordingly:

$$\begin{array}{llll} 1. \gamma = -1 & \gamma_1 = 0 & \gamma' = 1 & \gamma_1' = 0 \\ 2. \gamma = 0 & \gamma_1 = 1 & \gamma' = 0 & \gamma_1' = 1 \end{array}$$

The necessary conditions for equilibrium are:

<sup>1</sup> See M. Planck. Ueber die Vermehrung der Entropie. *Ann. der Phys. Wied.*, 32, 489, 1887.)

$$\begin{aligned} -\log c + \log c' &= \log K \\ -\log c_1 + \log c'_1 &= \log K_1, \end{aligned}$$

or, if it be taken into consideration that  $c$  and  $c'$  differ but little from unity, and if members of higher degrees be neglected:

$$\begin{aligned} c_1 - c'_1 &= \log K, \\ \text{and} \quad \log \frac{c'_1}{c_1} &= \log K_1. \end{aligned}$$

Only the first of these relations can be gotten into a form experimentally verifiable in the present state of our knowledge, and, accordingly, it alone will be treated of in this review.

$K$  is not a directly known function of temperature and pressure, and in order to get its expression in terms of those energy-factors, use must be made of the thermodynamic differential equation:

$$\frac{\delta (\log K)}{\delta p} = -\frac{V}{T}.$$

$V$  being the change of volume occasioned by the reaction at the temperature  $T$ ,  $\log K$  developed in a series according to powers of  $(p-p_0)$  becomes:

$$\log K = \log K_0 + (p-p_0) \left( \frac{\delta \log K}{\delta p} \right)_0 + \dots$$

The subscript  $(_0)$  indicates that for  $p$  the value  $p_0$  is to be placed; on account of the great dilution,  $(p-p_0)$  must be small, and hence all terms in the series can be neglected after the first power. If the term  $\frac{V_0}{T}$  be substituted for the differential quotient, the equation

$$c_1 - c'_1 = \log K_0 - (p-p_0) \frac{V_0}{T}$$

is obtained.

$V_0$  is the change of volume of the system, when, at the temperature  $T$  and under the pressure  $p_0$ , a gram molecule of the solvent vaporizes; accordingly we can put for it the molecular volume of the vapor, which is equal to  $\frac{RT}{p}$  by Boyle's and Gay-Lussac's laws; we then obtain

$$c_1 - c'_1 = \log K_0 - \frac{p-p_0}{p_0}.$$

$K_0$  depends only on the temperature and remains constant during isothermal changes of pressure. If we take  $p=p_0$ , we have to do with the pure solvent, and  $c_1$  and  $c_1'$  must be equal to zero, as well as  $\log K$  also; and generally we may put

$$c_1 - c_1' = \frac{p_0 - p}{p_0}.$$

In words this relation runs thus: "The relative depression of the vapor-tension is equal to the difference between the concentrations of the dissolved substance in the liquid and in the vapor."

Planck also got another expression for the differences between the concentrations ( $c_1 - c_1'$ ) in the following manner: If the equation  $c_1 - c_1' = \log K$  be developed in a series according to the powers of  $T - T_0$ , the series

$$\log K = \log K_0 + (T - T_0) \left( \frac{\delta \log K}{\delta T} \right)_0 + \dots \dots$$

is obtained. Treating this equation in a way similar to that taken in the previous case, and making use of the thermodynamic relation,

$$\frac{\delta(\log K)}{\delta T} = \frac{Q}{T^2},$$

we obtain the expression

$$c_1 - c_1' = (T - T_0) \frac{Q}{T_0^2},$$

where  $Q$  is the heat which is derived from the exterior, when a gram-molecule of the solvent vaporizes at the temperature  $T_0$  and under the pressure  $p$ . Planck accordingly enunciates this law: "The difference in the concentrations of the dissolved substance in the liquid and in the vapor is equal to the rise in the boiling point, divided by the square of the boiling point and multiplied by the molecular heat of vaporization of the solvent."

From experiments by Konowalow (*loc. cit.*) on mixtures of formic acid and water and of isobutyl alcohol and water, Planck calculated, according to his two formulas just given, the concentration in the gaseous phase, a satisfactory correspondence between the two sets of data being found.

Le Chatelier<sup>1</sup>, in his remarkable paper on chemical equilib-

<sup>1</sup> Recherches Experimentales et Théoriques sur les Equilibres Chimiques: Extrait des Annales des Mines de Mars-Avril, 1888, 281.

rium, devotes a section to the theoretical treatment of the vapor-tension of a mixture of liquids. The expression finally arrived at is quite complicated, and, although important results may be probably obtained by its applications, it is not expedient to enter into its development here.

A. Winkelmann<sup>1</sup>, in seeking experimental proof of the relations established by Planck (*loc. cit.*) between the composition of liquid mixtures and their vapors, condensed some of the vapors arising from a solution and ascertained the composition of the condensed vapors, or liquid by measuring its index of refraction. The experiments were made with mixtures of water and propyl alcohol; there is undoubtedly a correspondence between his experiments and Planck's theory, but it cannot be said to be very close.

Nernst<sup>2</sup> also has found an expression for the concentration of a volatile dissolved substance in the gaseous phase in terms of vapor-tensions. If  $n$  be the number of molecules of dissolved substance contained in  $N$  molecules of a solvent,  $k$  a factor of proportionality corresponding to the absorption coefficient of the dissolved substance, and  $p$  the partial pressure of the vapor of the dissolved substance in the saturated vapors over the solution, by Henry's law, the equation

$$Kp = \frac{n}{n + N}$$

may be formed. The vapor-tension of the solvent  $P$  is

$$P = P_0 \frac{N}{N + n}$$

where  $P_0$  is the vapor-tension of the pure solvent at the temperature in question.

According to Dalton's law, the total pressure of the saturated vapor  $\pi$  of the solution is

$$\pi = P + p$$

<sup>1</sup> Ueber die Zusammensetzung des Dampfes aus Flüssigkeitsgemischen: *Ann. der Phys. Wied.*, 39, 1-15, 1890.

<sup>2</sup> Vertheilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmittel und Dampfraum: Dampfspannungen verdünnter Lösungen flüchtiger Stoffe *Ztschr. Phys. Chem.*, 3, 124, 1891.

and the composition of the vapor may be shown to be

$$K \frac{n'}{N' + n'} = \frac{p}{P + p}.$$

Where  $N'$  and  $n'$  have the same significance for the vapor as  $N$  and  $n$  have for the liquid mixture.

Nernst gives in a little table a comparison of the data calculated by his formula with those obtained by the use of Planck's formula, both in turn being compared with the results of Winkelmann's experiments.

TABLE I.

*Mixture of 6.2 grams propyl alcohol and 93.8 grams water.*

<i>t</i>	<i>P<sub>0</sub></i>	$\pi$	<i>P</i>	<i>p</i>	$\frac{n'}{N' + n'}$	Per cent alcohol in vapor.		
						Winkelmann.	Nernst.	Planck.
17.65	15.0	20.8	14.7	6.1	0.293	....	58.0	64.2
31.5	31.3	....	30.7	....	....	52.3	59.4	66.0
40.3	55.7	79.4	54.6	24.8	0.312	57.4	60.2	67.2
51.0	96.7	138.7	94.8	43.9	0.316	60.8	61.9	67.7

It is apparent that Nernst's calculated data correspond better with the data observed than do those calculated by Planck's formula, although the correspondence in no case can be reckoned very close; it must be kept in mind, however, that Winkelmann's method is not very exact, and that the vapor-tensions and composition of distillates have been measured on chemical preparations from different sources. A difference, which may be called an advantage, between Nernst's and Planck's formulas, is that the former is not, like the latter, restricted to the consideration of dilute solutions only.

Nernst has also developed certain views in regard to the vapor-tensions of binary mixtures of volatile liquids.<sup>1</sup>

Taking as base of his considerations the empirical law: the vapor-tension of a liquid is lowered when a foreign fixed substance is dissolved in it; he states that this law is applicable also to solutions of volatile substance, only, in this case, the superincumbent vapor consists not of that of the solvent alone, but of a mixture of those of the dissolved liquid and of the solvent; the gaseous phase of the system contains both components of the so-

<sup>1</sup> *Theor. Chem.* 97, 1893, and *Siede und Schmelzpunkt*, 67, 1894.



lution, and according as the partial pressure of one component is greater or less than the diminution of the vapor-tension of the other which it causes by its presence, the total tension of the solution is greater or less. If now a small quantity of a liquid, A, be added to a liquid, B, the vapor-tension of B will be diminished proportionally to the quantity of A added; but the total pressure of the resulting solution will be increased, inasmuch as A as well as B gives off vapors, and the partial pressure of A is so much the greater as the solubility of the vapor A in the solution is smaller. According as the first or the second influence preponderates, the vapor-tension of the solution will be smaller or greater than that of the liquid B in a state of purity. Since the properties of such a mixture must vary continuously with the composition, the influence of the proportions of the two liquids upon the vapor-tension of the mixture may be considered under three cases.

1. The vapors of both A and of B are easily soluble in each other. If we add ever-increasing quantities of A to B the vapor-tension of the mixture will at first sink to a minimum and then rise, until, when a very great quantity of A has been added, it will approximate to that of the liquid A in a state of purity.

2. The vapors of A and of B are but slightly soluble in each other. If constantly increasing quantities of A be added to B, the vapor-tension increases, reaches a maximum, and decreases when a large excess of A has been added, to that of the pure liquid A.

3. The vapor of A is easily soluble in B, while the vapor of B is but slightly soluble in A. The addition of constantly increasing quantities of one liquid to the other causes the vapor-tension of the resultant mixture to pass without maximum or minimum from the vapor-tension of the second liquid to that of the first. But it is perhaps possible that the vapor of B in A is so difficultly soluble that the addition of a small portion of B to A elevates the vapor-tension, while at the same time the vapor of A is so easily soluble in B that by addition of A to B the vapor-tension is lowered. In that case, when B is added to A the vapor-tension increases at first, passes through a maximum, decreases to pass through a minimum, finally rising and approximating, when great excess of B is present, to that of the pure liquid B.

Recently, George U. A. Kahlbaum<sup>1</sup> and his assistants have determined according to the dynamic method the vapor-tensions at different temperatures of mixtures of water with formic and with acetic acid; also of mixtures of various acids of the fatty series. The determinations, which are very numerous, have been made by a method and with material undoubtedly capable of giving the best of results; it is to be regretted, however, that associated, instead of normal, liquids were taken.

It is seen in the foregoing historical sketch that only in the rarest cases have mixtures of normal liquids been investigated as to their vapor-tensions, and the partial pressures of the constituents of the vapor been determined. Now, as already stated on page 617, in order to get a full knowledge of the phenomena of vaporization of mixtures of volatile liquids, we must learn what the partial pressures of each is, when converted into vapor in equilibrium with the liquid phase; and we are the more likely to get clear ideas by investigating the simplest mixtures first, that is, mixtures made up of simple normal molecules. Having by considerations similar to these been led to take normal liquids to form the mixtures, the vapor-tensions of which are to be determined, my first task was to devise some experimental method, which furnishes a means of measuring the partial tensions of the vaporous members of a system of bodies. In order to do this, it is almost indispensable that the composition of the vapor be known, for, that being the case, it is easy to determine what part of the total pressure is to be attributed to each of its components. The problem then reduces itself to one of a simple analysis; but the difficulty is to get the vapor away from the liquid with which it is in equilibrium without its composition becoming changed during the operation. If the so-called static method of determination of vapor-tensions be adopted, it is possible by enlargement of the barometric vacuum to be filled by the vapor, and, after equilibrium has been attained, by separation of the liquid from the vapor by means of a stop-cock or other arrangement, to get enough of vapor to permit of its analysis. But a small amount can be obtained, however, and there is

<sup>1</sup> Studien über Dampfkraftmessungen. Basel, 1892.

great danger that the composition of the liquid mixture becomes considerably changed.

It is possible to collect some of the condensed vapor given off by a boiling mixture of liquids, and determine its composition, as did Duclaux in the paper cited above (page 620). Here, although it is easy to get a sufficient quantity of the condensed mixture of vapor to permit of quite accurate analysis,—provided that a method of analysis of the two liquids in question had been elaborated,—the change of concentration of the solution during the boiling as well as the concurrent change of temperature, together with the other disturbing circumstances, render the accuracy of such work rather illusory.

Accordingly, another means of determination of vapor-tensions had to be found for the purpose of this investigation; and, indeed, the method founded upon the determination of the quantity of a volatile liquid carried off by a definite volume of an inert gas made to pass through it, and the direct subsequent analysis of the gaseous mixture, either by passing it through appropriate liquid absorbents, such as an alkali, where one of the components of the gaseous mixture is an acid, or over decomposing agents, such as red-hot lime, etc., in case one of the components contains sulphur or a halogen, has been adopted; the method, be it said right here, has been found to meet the requirements of the investigation in a satisfactory manner. It is, indeed, true that the variety of the liquids which can be subjected to investigation is limited, for one member of a mixture must needs be a liquid containing a halogen or sulphur atom, or an acid. Still it is possible to find enough such liquids of differing functions that the results obtained by them can without question be transferred to mixtures made up of any normal liquids whatsoever, and any conclusions drawn, become general.

### 3. DESCRIPTION OF APPARATUS.

It is of prime importance in the determination of vapor-tensions that the temperature be kept uniform; accordingly I describe, first of all, the apparatus employed for that purpose.

*Thermostat.*—This consisted of a cylindrical copper vessel holding nearly forty liters of water. It was heated by means of

a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald,<sup>1</sup> controlled the combustion of the gas. To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure. Such a means of agitation gives very satisfactory results; it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within  $0.05^{\circ}$  during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the "Physikalische Reichsanstalt" of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory. The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapor of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

*First Principal Part of Apparatus.*—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying-tubes. I pass to the description of each.

*The Measuring Vessel* consists of an ordinary bottle of a capacity varying from one to three liters, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a T tube. This branch of the T tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about three inches. The wider branch of the tube is

<sup>1</sup> *Ztschr. phys. Chem.*, 2, 565, 1888.

pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened, water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half cc. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapor-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

*The Pressure Regulator* consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stop-cock at its upper end; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T tube, of which one of the horizontal

branches is connected by means of a bit of stout rubber with the narrower branch of the T tube belonging to the measuring vessel, while the other is attached by rubber tubing to the other parts of the apparatus. If water be run into the bottle serving as pressure regulator, the air in it is compressed until it can force itself through the liquid with the vapor of which it is to be saturated.

*The Manometer* is intended to measure the amount of this compression or the internal pressure; it is made of ordinary glass tubing bent into U shape, with the branches about two feet long. It may be put between the measuring vessel and the pressure-regulator, or between the drying tubes and the latter; I have found it most convenient, however, to melt it into the vertical branch of the T tube of the measuring vessel just opposite the horizontal branch, as shown in Fig. 1. The manometric liquid is water, and the differences of the heights of the liquid columns of the two branches, is read to a millimeter by means of a metric rule; the readings are then easily exact to a tenth mm. of mercury.

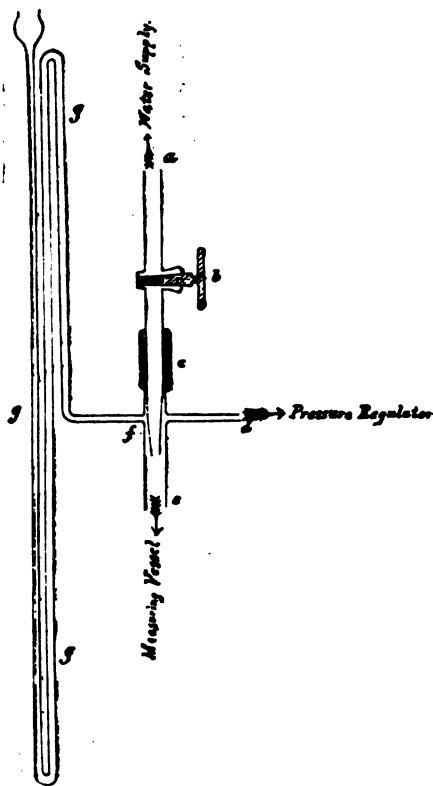


FIG. 1.

and filled with various drying agents. Liquids, such as strong sulphuric acid, must be rejected, however, as they increase the internal pressure, and often cause an irregularity in the flow of the gas. I found U tubes to be the best shape, and grains of

*The Drying Tubes* can, of course, be of various shapes

pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least sixty centimeters is to be taken, and the pumice must be changed often. When it becomes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda lime is taken. At the end of the last U tube, a mercury valve is attached to prevent the backward diffusion of the vapors; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

*Second Principal Part of Apparatus.* This is the absorption vessel, which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand sometime before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the thermostat; the case had holes in its sides, below the surface of the water, for the conduction and abduction of air, platinum capillaries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfactory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmosphere of which was kept dry by means of concentrated sulphuric acid.

*Third Principal Part of Apparatus.*—In order to analyze the mixture of vapors issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the sec-

ond, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given:

(1) The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a U tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy and hence steady retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a T tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

(2) This analyzing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

*Performance of an Experiment when the Mixture Contains an Organic Halogen or Sulphur Compound.*—The hard glass tube (about eighty cm. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the U tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a



current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure-regulator, and the system of drying-tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the U tube (of course, no air is now being passed through the analyzing tube), and after a couple of minutes of half submersion in the bath, it is attached to the system of drying tubes. It is now wholly submerged in the bath and air is made to pass through it as follows :

The stop-cock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stop-cock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a liter an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than one or two mm. of water, or less than one-tenth mm. of mercury.

The barometer is also read off at the beginning and at the end of the experiment; in all my determinations, the difference of the two readings was less than one mm. of mercury.

A minute or so before the measuring vessel is full, the absorption bulbs are lifted out of the water enough to bring the end tubes about two inches above the surface, and there, together with the joining tube on one side and the cork and end of U tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the T tube (level of cork), the absorption vessel is detached from the dry-

ing tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation, the connection between the absorption vessel and the U tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained is fitted into the U tube, its object being to prevent the escape by diffusion of any portion of vapor contained in the U tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapor to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes; in a well conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube or if the dilute nitric acid in the Maquenne absorption bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down, the lime tube is removed and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added, if necessary. If more than a half gram of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate; some, also, were analyzed volumetrically, Volhard's method being employed.

*Performance of an Experiment when the Mixture contains an Acid.*—The absorption vessel is filled with the mixture being

investigated, and weighed as described above. It is then joined by means of a good cork to the analyzing apparatus, into which are run from a pipette ten cc. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralize the vaporized acid. The further end of the analyzing arrangement is closed with a U tube filled with soda lime so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analyzing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in communication with the drying tubes, etc., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air and the barometric height. A slight correction has to be made to the barometric reading for the following reason: after the air passes the liquid contained in the absorption vessel and comes into the analyzing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corresponding to the difference of level between the two surfaces of the alkaline solution; this, in my apparatus, was determined to be equal to one mm. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stop-cock, through which water enters into the measuring vessel, is closed, the absorption and analyzing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapors in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stoppered and set in the balance-case, while the contents of the analyzing vessel are poured into a beaker, rinsing being done with water free from carbon dioxide. Without delay, the excess of alkali is estimated by titration against deci-normal acid solution, and by a simple calculation, the quantity of evaporated acid is obtained.

#### 4. CALCULATION OF RESULTS.

In the calculations it is assumed that the laws of perfect or ideal gases may be applied to the mixtures of vapors; that is, the laws of Boyle, Gay Lussac, and Dalton. Where not too much vapor is present in the gaseous mixture the legitimacy of this assumption is unquestionable; and even though this condition be not fulfilled, the approximation to accuracy may be sufficient (see section 6).

*Calculation of Volume of Air Passed Through a Mixture.*—In order to force the air in the measuring vessel through the liquid in the absorption vessel, it is necessary that it be brought under a pressure equal to that of the atmosphere plus that required to vertically displace the liquid contained in the bulbs, the latter pressure varying with the density and amount of the mixture. The volume of the air under atmospheric pressure may be obtained then as follows:

Let  $P$  represent the pressure of the atmosphere. Let  $P'$  represent the pressure which forces the air through the liquid. Let  $V'$  represent the volume of air under the pressure  $P + P'$ . Let  $V$  represent the volume of air under the pressure  $P$ .

According to Boyle's law, and inasmuch as the temperature remains constant,

$$V = \frac{(P + P') V'}{P}$$

*Calculation of Composition of Mixture of Liquid Vaporized.*—As this calculation is simply one of quantitative analysis, it is not necessary to treat of its details.

*Calculation of Partial Volumes of Mixtures of Vapors.*—Let  $m$  represent the quantity of one component in the gaseous mixture. Let  $M$  represent its molecular mass. Let 22.32 represent the volume in liters of a gram-molecule of hydrogen at the tem-

perature  $0^\circ$  and under the pressure 760 mm. Let  $\alpha$  represent the coefficient of expansion. Let  $v_1$  represent the volume of vapor at the temperature of the determination  $t$  and under the atmospheric pressure  $p$ . We then have

$$v_1 = 22.32 \frac{m}{M} \times \frac{760(1 + \alpha t)}{p}.$$

*Calculations of Partial Pressures of Components of Vapor Mixture.*—Let  $v_1$  represent partial volume of one component. Let  $v_2$  represent partial volume of the other. Let  $v$  represent partial volume of air. Let  $p_1$  represent partial pressure of one component. Let  $p_2$  represent partial pressure of the other. Let  $p$  represent the atmospheric pressure.

In accordance with Dalton's law,

$$p_1 = p \frac{v_1}{(v + v_1 + v_2)}$$

and

$$p_2 = p \frac{v_2}{(v + v_1 + v_2)}.$$

##### 5. DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In order to make a just estimate of the degree of accuracy attainable by the above described apparatus, it is necessary to consider somewhat in detail the possible sources of error that may accompany a determination of the vapor-tension of a liquid made by it.

*Error in Measurement of Volume of Air Passed Through the Absorption Vessel.*—At the beginning of an experiment, both surfaces of the liquid under examination are under atmospheric pressure; by compression of the air in the reservoirs and drying tubes it is forced through the system of bulbs of the absorption apparatus. If, in all experiments, the same volume of liquid be taken, the amount displaced will be the same, and the internal pressure will be greater or less, according as the liquid employed is more or less dense. The internal pressure in some determinations varies slightly during their performance; the variation, however, never exceeds a millimeter or so of mercury. The use of a column of water to measure the internal pressure renders its determination very exact. The atmospheric pressure was found

to remain practically constant during an experiment, which seldom lasted more than an hour and a half. The error arising from the determination of the pressure to which the air in the interior of the apparatus is subjected, can accordingly be reckoned so slight as to be entirely negligible.

The mercury filled into the measuring vessel for the ballast, as well as the volume of water used to calibrate the same, can be measured to within a half cc., and as from 100 to 300 cc. of mercury and 1,000 to 3,000 cc. of water were taken, the error committed cannot be more than a thousandth of volume of air, and, in most cases, is probably less.

The air is, from the way it is forced from the measuring vessel, always measured when saturated with aqueous vapor. The drying tubes are always to be so filled with the drying reagents as to leave as little room as possible; I found, however, by special experiments, that the shape and size of the drying tubes exercise no appreciable influence upon the quantity of liquid carried off by the air; the only requisite seems to be that they dry the air thoroughly.

All the parts of the apparatus employed in measuring the volume of air being completely submerged in the water of the thermostat, there is no possibility of error arising from non-uniformity of temperature. The temperature of the water which expelled the air was, in most of my experiments, about  $20^{\circ}$  lower than that of the thermostat, but it entered the measuring vessel so slowly that it took on the temperature of the bath without disturbing, to any appreciable degree, the prevailing thermal conditions. That the water introduced took on rapidly the temperature of the bath was proven by the circumstance that, when, at the end of a determination, the flow of the water was stopped, and the level of the letter was flush with the gauge-mark, if the measuring vessel, which in this condition might be said to be a rude but still quite delicate thermometer, was allowed to stand undisturbed for some time, no expansion or, at most, but very slight expansion of the water occurred.

*Error from Change of Concentration of Mixture.*—A source of error is to be found in a possible change of the concentration caused by one or the other of the components of the mixture

being carried off by the air in such quantity that the composition of the residual mixture is not the same as at the beginning of an experiment; I think, however, that the error introduced in this manner is so slight as to be practically negligible, and for the following reasons:

1. The shape of the absorption vessel is such as to form five chambers almost entirely independent of one another as far as their contents are concerned. The stream of air becomes saturated in passing through the first two or three bulbs, and passes through the last two without changing, to an appreciable degree, the composition of the mixture contained in them. That saturation is complete after the air has been passed through the first three bulbs, I assured myself by special experiments; that is, I filled only the three first bulbs, and found, on passing a certain volume of air through them, that the evaporated quantity of liquid was the same as when the same volume of air under similar conditions was passed with all the bulbs filled with the liquid.

2. As from forty to eighty grams of solution were taken in a determination, and as the quantity evaporated rarely exceeded two grams, it is evident that, even if, towards the last of the experiment, the concentration of the first bulb had altered somewhat, the composition of the mixture in the fifth bulb would remain practically unchanged.

3. Most of the mixtures examined were made up of liquids possessing not greatly different vapor-tensions, so that the vapors of both liquids passed off in about the same proportions.

*Error in Analysis of Mixture of Vapors.*—The mixture of vapors on escaping from the absorption vessel passes into the U tube, and thence through the lead tube into the analyzing tube. In order that no vapor may condense in the end of the U tube flared out for the reception of the cork through which passes the outlet tube of the bulb apparatus, the latter tube is ground into the horizontal branch which is somewhat constricted for that purpose; the cork is employed to give solidity and stiffness to the juncture. It is believed that by this means all the vapor passes into the horizontal branch of the U tube where it is directly exposed to the action of the entering current of air.

Necessarily, the outer branch of the U tube has to project a little out of the water of the bath in order that the lead tube may pass over the side of the thermostat; hence, as the upper part and the lead tube are generally at lower temperature than the water of the bath, some condensation of the vapors occurs; the condensed vapor runs down the tube to collect at the bottom. In order to vaporize this liquid and cause it to pass over the glowing lime, it is necessary to pass a current of air through the tubes to complete the determination. In this operation, two sources of error may be encountered: First, when the connection between the absorption vessel and the U tube is broken, some of the vapor with which the tubes are filled may diffuse out and be lost; and second, the vapor may be carried along too rapidly with the air to permit of its complete decomposition by the heated lime. There seems to be no simple means of avoiding slight loss of vapor; still, by careful manipulation and rapid operation, the loss may be rendered insensible.

My mode of operation was as follows: Holding between the thumb and first finger of my right hand the little stopper of the absorption vessel, and between the thumb and the first finger of my left hand the cork and tube to be fitted into the horizontal branch of the U tube, I withdrew the cork, and at once inserted in the U tube the cork and tube. The time that the ends of the pieces of apparatus were open was less than two seconds, so that the loss must have been minimal.

A circumstance which aids in the prevention of loss by diffusion is, that the heated lime tube causes a slight draft towards it when the U tube is open. It is certainly legitimate to conclude that the error from this source is exceedingly slight.

In regard to the second source of error the greatest precautions must be taken to prevent its assuming disturbing proportions. As soon as the connection between the absorption vessel and the U tube has been secured, the pinch-cock on the end of the rubber tubing (see page 633) is closed a little so that air is drawn in a slow stream through the tubes at first, and faster afterwards (see page 634). The amount of error due to this source is best determined by special experiments in which a weighed quantity of a pure halogen compound is introduced



into the absorption vessel, a certain volume of air passed through it, all the usual precautions in determining a vapor-tension being observed, and a comparison made between the loss by vaporization and the amount of the compound calculated from the quantity of halogen found in the lime; naturally the loss should, in case no error of experimentation has occurred, be equal to the quantity of liquid corresponding to the halogen found by analysis. Two experiments were carried out, one with carbon tetrachloride, and the other with chloroform. The difference between the weights and the liquids before and after the passing of the air was for chloroform 1.9014 grams, and for carbon tetrachloride 2.0178 grams; the results of analysis gave the amount of chloroform to be 1.9022 grams and that of carbon tetrachloride 2.0167 grams. As is seen, the differences between the two sets of results are not more than those due to the errors of analysis, and it seems that the error due to the analysis of the mixture of the vapors is very slight.

When an acid is in the mixture whose vapor-tension is being determined, the error attendant upon the determination of the amount vaporized cannot be more than that incurred in a titration, since there is no chance for the acid to escape, so quickly and directly is it brought in contact with the absorbing alkaline liquor. In a special experiment, the loss of acid from the absorption vessel was 0.2908 grams, while a titration of the solution of baryta gave as the amount of acid 0.2896 grams.

While the errors of the experimental method here described seem to be slight, there is an error that may have been committed in the assumption which lies at the basis of our calculations; when the volume of a vaporized liquid is large in comparison with the total gaseous volume, it is very probable that the vapor cannot be likened even approximately to an ideal gas. This point will be discussed in the following section.

#### 6. COMPARISON OF THE VAPOR-TENSIONS OBTAINED BY THE METHOD HEREIN DESCRIBED AND THOSE OBTAINED BY OTHER METHODS.

Probably the best way to judge of the accuracy of the results

obtained in the determination of the vapor-tensions of liquids according to the method described in this paper is to compare them with the results obtained by other investigators working by other methods. Also a criterion of accuracy is to be found in the more or less close concordance of duplicate experiments. In the following table are given the necessary data of my experiments together with the results obtained by others. It was in some cases necessary to interpolate the results of others inasmuch as my results referred to a limited number of temperatures; the interpolations were made on a large scale, so as to avoid any slight inaccuracy. The original papers of Young and Regnault I am now unable to consult, and have to take their data as given in Landolt and Börnsteins "Physikalisch-Chemische Tabellen" or other reproductions.

TABLE II.<sup>1</sup>  
*Vapor Tensions of Pure Liquids.*

Name of liquid.	Temperature.	Loss in grams.	Volume of loss in cc.	Volume of air in cc.	Internal pressure in mm. Hg.	Barometer in mm. Hg.	Tension of vapor in mm. Hg.	Tension according to other observers.
Benzene.....	34.8°	1.3805	443.	1876	5	760	145.4	147.2 (Y)
Monochlorbenzene ..	34.8°	0.2291	5.1	1883	10	757	20.3	20.0 (Y)
Monobrombenzene ..	34.8°	0.1289	2.0	1888	10	757	8.0	8.0 (Y)
Toluene.....	34.8°	0.2451	67.6	1014	11	754	46.8	
" .....	34.8°	0.4672	128.9	1949	11	754	46.7	
Metaxylene (not especially purified) ..	34.8°	0.1080	25.8	1201	17	757	4.17	
Metaxylene (not especially purified) ..	34.8°	0.1085	25.9	1201	17	758	4.18	
Nitrobenzene.....	34.8°	0.0090	1.85	1210	23	757	1.16	
" .....	34.8°	0.0088	1.83	1207	21	757	1.15	
Carbon tetrachloride.	34.8°	3.3803	5.55	1913	20	758	169.4	172.6 (R)
" .....	27.8°	2.4031	3.96	1908	18	756	130.0	130.8 (R)
Chloroform .....	35.0°	3.0320	64.48	1033	25	755	290.1	301.1 (R)
Ethyl iodide .....	34.8°	4.2091	683.	1913	20	756	199.0	206.0 (R)
" .....	27.8°	2.9760	483.	1918	22	756	152.2	154.7 (R)
Carbon bisulphide...	20.0°	2.4541	777.4	1206	21	756	296.4	298.1 (R)
Methyl formate .....	20.0°	5.1090	195.8	1196	16	756	469.4	
Acetic acid .....	35.0°	0.2900	70.0	1960	20	760	26.3	26.5 (R & Y)

An inspection of the table shows a most excellent correspond-

<sup>1</sup> Bibliographical references to Table II: (Y)=Young; Chem. Soc. 55, 486, 1889. (R)=Regnault: Mémoires de l'Académie, 26, 239, 1862. (R & Y)=Ramsay & Young, Chem. Soc., 49, 790, 1886.

ence between my determinations of vapor-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution products of benzene. But when, at the temperature taken for a determination, the elastic force of the vapor exceeds one hundred mm. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapor-tensions were carried out at two different temperatures. For carbon tetrachloride the difference between Regnault's results and mine is three and two-tenths mm. of mercury at  $34.8^{\circ}$  and eight-tenths mm. of mercury at  $27.8^{\circ}$ ; for ethyl iodide, the difference at  $34.8^{\circ}$  is seven and one-tenths mm. of mercury, and at  $27.8^{\circ}$  one and five-tenths mm. of mercury. Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in the last paragraph of the discussion of the errors to which this method is subject. The assumption, made in the calculations, that the vaporous mixture may be treated as a mixture of ideal gases, cannot be maintained when the volume of the vaporized liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel. The vapor of ethyl iodide that was carried off by the air, occupied more than a fourth of the total volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapors of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid. And, as has been shown, the less volatile liquids give results perfectly concordant with those obtained by others. Duplicate determinations of the vapor-tensions of some of the liquids, as toluene, nitrobenzene, etc., give almost identical results.

It would not be difficult to apply a correction taking into account the greater volatility of some of the liquids. This I have not, as yet, done, as in certain details I wish to alter the apparatus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring

vessel would render the system of drying tubes unnecessary; also ground glass joints are undoubtedly preferable to rubber connections. Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have in the case of the more volatile liquids the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapor-tensions of mixtures of liquids, since both liquids, if their vapor-tensions be not too different, are affected alike by any weaknesses in the method, and the phenomenon observed permits of the drawing of theoretic conclusions. Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than one mm. of mercury when the vapor-tension does not exceed 100 mm. of mercury, and to less than two mm. of mercury when the vapor-tension is less than 150 mm. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within two mm. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

#### 7. CHOICE AND PURIFICATION OF LIQUIDS.

As stated previously, the liquids employed in the course of this investigation were those recognized to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity. The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of apply-

ing the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapor-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

*Benzene*.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallized until about a pound was obtained melting at  $5.3^{\circ}$ . This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling point  $80.1^{\circ}$  under a pressure of 756 mm. of mercury being observed. Its specific gravity at  $25^{\circ}$  referred to water at the same temperature was found to be 0.876611.

*Toluene*.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at  $109.8^{\circ}$  to  $110.1^{\circ}$ , an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at  $110.1^{\circ}$  under a pres-

sure of 758 mm. of mercury. Its density at 25° referred to water at 25.0° was ascertained to be 0.86288.

*Monochlorbenzene*.—A couple of pounds of monochlorbenzene were repeatedly distilled in fractions until a constant boiling product resulted. About three-quarters of a pound were obtained, boiling at 131.8° to 131.9° under a pressure of 757 mm. of mercury, and having a density at 25.0° (referred to water at same temperature) of 1.10362.

*Monobrombenzene*.—Nearly a pound of brombenzene was fractionally distilled until a distillate was obtained boiling between narrow limits. About 150 grams of the product, boiling at 154.3° to 154.5° under a pressure of 761 mm. of mercury were obtained. The density at 25° referred to water at 25.0° was 1.49852.

*Nitrobenzene*.—The commercial article was repeatedly crystallized until an almost colorless liquid was obtained, which when solidified, showed the same temperature during the remelting. It possessed a melting point of 3.6°, and its density was 1.20201,  $\left(\frac{25^\circ}{25^\circ}\right)$ .

*Chloroform*.—About two pounds of "chloroform anesthetique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled. The larger distillate boiled at 60.8° to 61.0° under a pressure of 751 mm. of mercury, and finally nearly a pound was obtained boiling at 60.9° under a pressure of 755 mm. of mercury.

*Carbon Tetrachloride*.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then rectified, and nearly a pound boiling throughout the operation at 76.6° under a pressure of 756 mm. of mercury taken for the preparation of the mixtures. The specific gravity of this product at 25.0° referred to water at the same temperature was 1.58828.

*Acetic Acid*.—Two pounds of glacial acetic acid were repeatedly fractionally crystallized until a portion melting at 16.7° was obtained. The bottle containing it as well as the mixtures made

from it were kept under an air-tight bell-jar by the side of very strong sulphuric acid.

#### 8. PREPARATION OF THE MIXTURES.

The mixtures were prepared by weighing out to a milligram on a balance turning with a tenth milligram the liquids in a flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, the composition of the liquid was thus known to a ten-thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry, cool, dark closet. As, almost invariably, the necessary vapor-tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius' method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. Five to ten cc. of the mixture were carefully weighed out in a glass-stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardized baryta water run in to point of neutralization. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

#### 9. EXPERIMENTAL RESULTS WITH MIXTURES OF NORMAL LIQUIDS.

In the following tables (III to X) are given those data of the experiments necessary for the calculation of the vapor-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary. In some cases, the data have been represented graphically. (Figs. II. to IV.)

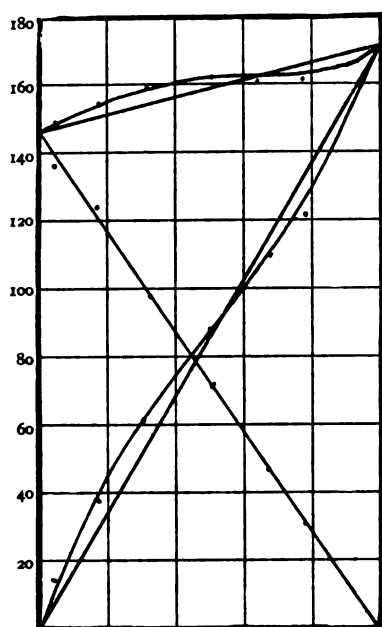


FIG. 2.

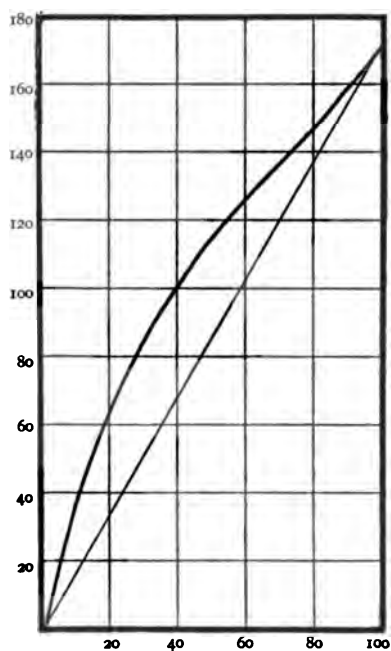


FIG. 4.



FIG. 3.



## EXPLANATION OF FIGURES.

Fig. 2.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CCl}_4$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 3.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CHCl}_3$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 4.—Vapor-tensions of mixtures of nitrobenzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CCl}_4$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

TABLE III.

*Vapor-Tensions of Mixtures of Benzene and Monochlorobenzene at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Chlorobenzene at 34.8° is 20.3 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Cl}$ in vapor.	Grams $\text{C}_6\text{H}_6$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Cl}$ in mm.	Ten- sion of $\text{C}_6\text{H}_6$ in mm.	Vol- ume of air in mm.	Barom- eter in mm.	Inter- nal pressure in mm.
15.18	1.33	0.0454	2.3075	1.7	124.6	3782	763	11
29.08	6.11	0.0857	0.9143	6.6	101.3	1900	757	17
65.06	19.37	0.1800	0.5202	12.3	51.3	2032	758	18
79.21	35.15	0.3572	0.4750	19.1	27.9	3787	756	12

TABLE IV.

*Vapor-Tensions of Mixtures of Toluene and Monochlorobenzene at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Chlorobenzene at 34.8° is 20.3 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Cl}$ in vapor.	Grams $\text{C}_7\text{H}_8$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Cl}$ in mm.	Ten- sion of $\text{C}_7\text{H}_8$ in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
18.96	9.84	0.0510	0.3821	4.3	38.2	1963	757	17
41.82	22.66	0.0985	0.2754	8.1	27.6	1973	760	21
76.71	67.79	0.2089	0.0821	17.5	8.2	1965	757	18

TABLE V.

*Vapor-Tensions of Mixtures of Benzene and Monobromobenzene at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Bromobenzene at 34.8° is 8.0 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Br}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Br}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Br}$ in vapor.	Grams $\text{C}_6\text{H}_6$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Br}$ in mm.	Ten- sion of $\text{C}_6\text{H}_6$ in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
30.33	24.30	0.0395	0.4975	2.6	103.1	1018	757	13

TABLE VI.

*Vapor-Tensions of Mixtures of Benzene and Chloroform at 34.8°.**Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.**Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.*

Molecules CHCl <sub>3</sub> in 100 mole- cules of liquid mixture.	Molecules CHCl <sub>3</sub> in 100 mole- cules of gaseous mixture.	Grams CHCl <sub>3</sub> in vapor.	Grams C <sub>6</sub> H <sub>6</sub> in vapor.	Ten- sion of CHCl <sub>3</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>6</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
16.97	24.30	0.3243	0.6607	39.6	123.5	1032	755	25
50.53	63.74	1.1513	0.4187	130.7	74.3	1030	756	25
59.47	73.25	1.4770	0.3531	162.2	59.2	1030	749	25

[TO BE CONTINUED.]

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. NO. 2.]

## THE ELECTROLYTIC DETERMINATION OF RUTHENIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received April 22, 1895.

FROM time to time efforts have been made in this laboratory to gather information upon the deportment of the metals of the platinum group toward the electric current. Palladium, platinum, and rhodium have been determined quantitatively, and also separated electrolytically from other metals of the group, *e. g.*, palladium from iridium. The purpose of this communication is to present data relating to the electrolysis of ruthenium salt solutions. The literature of electrolysis does not contain any information upon this point.

The salt upon which the experiments were made was the double chloride of potassium and ruthenium. It was prepared by fusing the finely divided metal with potassium nitrate and hydroxide. This fusion was made in a silver crucible. The aqueous extract was acidified with hydrochloric acid, and the solution was then evaporated to crystallization. Much potassium chloride separated at first, but finally the double salt appeared in minute red-colored needles.

The platinum dish in which the electrolytic decomposition was carried out was coated upon its inner surface with a layer of copper. In the first trials the solution of the double salt was mixed with three grams of sodium acetate, and acted upon by a current of N. D.<sub>100</sub> = 0.01–0.05 ampere. The quantity of the ruthenium salt not being very abundant it was necessary to conduct the determinations with rather small amounts of material.

Thus, fifty cc. of the double chloride solution contained 0.0593 gram of ruthenium metal. The results of four trials were:

1 .....	0.0119 gram of ruthenium in five cc. of solution, equal to 0.0595 gram in fifty cc.
2 .....	0.0589 gram in fifty cc. of solution.
3 .....	0.0593 " " " "
4 .....	0.0590 " " " "

The metal deposit in each instance was dull black in color. A tendency to sponginess was also observed.

As other metals of the platinum group had been precipitated successfully from a phosphate solution (*Am. Chem. J.*, **13**, 206) ruthenium was tried under similar conditions.

In the experiments that follow, fifty cc. of the salt solution contained 0.0407 gram of metal. Fifteen cc. of disodium phosphate (1.0358 sp. gr.) and one cc. of phosphoric acid were added to this solution. The current was of the same strength as that used in the first series of experiments. The metallic deposits weighed:

1 .....	0.0402 gram.
2 .....	0.0407 "
3 .....	0.0413 "

The ruthenium in each instance was bright and steel-like in appearance. It was also very adherent. There was not the slightest indication of sponginess. In the two series just given the deposit of metal was washed first with warm water, and subsequently with absolute alcohol. The period of precipitation continued through the night, although six hours were found to suffice for the complete deposition of the ruthenium.

In a third series of two trials, fifty cc. of the salt solution contained 0.0100 gram of ruthenium. The phosphate, phosphoric acid, and the current were the same as in the series immediately preceding. Results:

1 .....	0.0101 gram ruthenium.
2 .....	0.0100 " "

The deposits, as before, were bright and apparently crystalline.

Mention has already been made that palladium and platinum could be separated electrolytically from iridium (*Am. Chem. J.*, **16**, 435) when present together with the latter in a phosphate solution. This was, however, not found possible with rhodium, although this metal was successfully deposited from a similar

solution. As ruthenium, from the results just given, allies itself with palladium, platinum, and rhodium, so far as its deposition from a phosphate solution was concerned, it seemed of interest to ascertain whether a separation of it from iridium could be effected.

*Separation of Ruthenium from Iridium.*—Here again a solution of ruthenium was used in fifty cc. of which there was 0.0100 gram of ruthenium. To this were added ten cc. of an iridium solution (equal to one-tenth gram of iridium), ten cc. of disodium phosphate, 1.0358 sp. gr., and three cc. of phosphoric acid. The current was  $N. D_{100} = 0.01$  ampere. It acted through the night. The deposit of ruthenium in each of the three experiments was bright, metallic, and perfectly adherent. It was washed and dried as in the determinations described in the preceding lines. Results:

1.....	0.0104	gram of ruthenium.
2.....	0.0096	" " "
3.....	0.0100	" " "

Additional experiments on the separation of the two metals were made with similar results.

It would be of interest and value to study the conduct of ruthenium in alkaline solutions. Wöhler<sup>1</sup> observed that the metal could be quickly brought into solution when the current acted upon it in the presence of an alkali. It is altogether probable that, under such conditions, its separation from the other metals of the group could be quite readily brought about, but lack of material will, at least for the present, prevent any such investigation.

UNIVERSITY OF PENNSYLVANIA.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 3.]

### THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON THE DIOXIDES OF ZIRCONIUM AND THORIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received May 31, 1895.

SOME years ago Weber (*Jahr. 1859, 77*) studied the action of phosphorus pentachloride upon inorganic oxides, such as those of silicon, titanium, and tin, and demonstrated that the

<sup>1</sup> *Ann. Chem. (Liebig)*, 146, 375.

products of the reaction were the corresponding metallic chlorides, together with phosphorus oxychloride. Tüttschew (*Jahr.* 1867, 205), working upon titanium dioxide with a modified method, obtained a double chloride corresponding to the formula  $\text{TiCl}_4 \cdot \text{PCl}_5$ .

It seemed to us of some interest to extend the study to the oxides of zirconium and thorium, thus completing the reaction with the more metallic bodies of Group IV of the periodic system. The procedure adopted by us consisted in introducing ignited and pure zirconium dioxide with its equivalent of phosphorus pentachloride into hard glass tubes, which were sealed after the air had been exhausted from them. The reaction appeared not to occur at  $150^\circ \text{C}$ ., but after heating to  $190^\circ \text{C}$ ., for a period of eight hours, a complete change was observed. A crystalline mass was noticeable and drops of phosphorus oxychloride were scattered through the tubes. These were opened at both ends and quickly connected with a chlorine generator, and distillation carried out by careful heating in an air-bath. Phosphorus oxychloride and some pentachloride were expelled. At  $190^\circ \text{C}$ ., crystals made their appearance in the cooler part of the tube, projecting beyond the air-bath. These were transparent and almost half an inch in length. That portion of the tube in which they had collected was severed, tightly closed, and weighed. It was then introduced into water. A hissing sound was quite distinct. Zirconium hydrate soon separated. After standing a while this was dissolved in dilute nitric acid, and reprecipitated with ammonia. Later it was found that to let the weighed chloride slowly absorb moisture from the air and then bring it into water insured better results. The percentage of zirconium found equaled 37.52 per cent., while the chlorine was 61.62 per cent. The theoretical requirements for the tetrachloride are 38.79 per cent. of zirconium and 61.21 per cent. of chlorine. Our zirconium result is low, yet the figures from three or four analyses concord so closely that there can be no question as to the correct nature of our product. A compound of zirconium chloride with either phosphorus pentachloride or oxychloride would require decidedly less zirconium and more chlorine. Hence, we can safely conclude that with our conditions

of experiment phosphorus pentachloride changes zirconium dioxide to the corresponding chloride. Thorium dioxide was subjected to a similar treatment. The temperature, however, at which the reaction seemed to proceed almost to completion was about  $240^{\circ}\text{C}$ . Exactly the same course was pursued in subsequently eliminating the excessive phosphorus compounds. The product analyzed showed the presence of a little phosphorus, not enough to establish the existence of a double chloride, therefore its quantity was deducted from the quantity of material used in the analysis. The thorium found equaled 62.23 per cent. and the chlorine 38.37 per cent., while the theoretical requirements for thorium tetrachloride are 62.23 per cent. thorium and 37.77 per cent. chlorine.

Our experiments supplement the investigations of Weber and justify the general inference that the dioxides of all the metallic members of Group IV are changed to tetrachlorides when heated under pressure with phosphorus pentachloride.

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### NEW BOOKS.

A TEXT-BOOK OF CHEMISTRY INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. BY SAMUEL P. SADTLER AND HENRY TRIMBLE. Octavo, pp 950. Philadelphia: J. B. Lippincott & Co., 1895.

The title on the cover is "Pharmaceutical and Medical Chemistry," from which it is to be regretted that the authors did not omit the word "Medical," as its use compels a remonstrance against the view which they apparently entertain, that the needs of the medical student in the department of chemistry do not extend beyond the study of the properties of drugs and the methods of chemical manufacture. Physiological, hygienic and toxicological chemistry are almost utterly ignored. A mere outline of the chemistry of urea is compressed into less than a page, while more than two pages are devoted to alizarin. Serum albumen is dismissed in four lines, without a word about the testing of urine for albumen. The discussion of the degrees of purity of natural waters is barely hinted at in a few lines, without any reference to the methods of examination of water, even

in the part devoted to analytical chemistry. The space allowed to the toxicological chemistry of arsenic is only three-quarters of a page, while the metallurgy of iron occupies four and three-quarter pages. To designate such a work as a "Medical Chemistry" is, to put it mildly, a misnomer.

Viewed, however, as a text-book for the use of the student of technical chemistry or the manufacturing pharmacist, the work is, in most respects, well arranged and, in the main, up to the times, although in some points somewhat too conservative. Such terms as acid potassium sulphate, copper sulphate, calcium phosphate, sodium sulphate, acid calcium phosphate, either have the ring of antiquity or lack precision. The orthography endorsed by the A. A. A. Sc. has not been adopted.

The work is divided into five parts. Part I contains, in 90 pp., a brief outline of elementary physics, which is rather popular and general than chemical or medical. The laws of Dulong and Petit and of Raoult are not mentioned, absorption spectra are merely referred to, and the description of the errors of refraction of the eye is not only fragmentary but misleading.

Parts II and III (182 and 243 pp.) treat of mineral chemistry. The elements are classified into "non-metals" and "metals," a division which widely separates nitrogen and phosphorus from their close relations to arsenic and antimony. Methane, ethane, acetylene, and the oxides and sulphides of carbon are treated of as universal substances in Part II. Descriptions of the methods of preparation of the elements and their compounds, and statistics of industrial production are detailed and illustrated by numerous familiar cuts of furnaces and other forms of manufacturing plants. Pharmaceutical references are in accordance with the last revision of the U. S. Ph.

Part IV (280 pp.), devoted to organic chemistry, is admirably written. The arrangement is logical and scientific, and the matter is abreast of the advances in this most important division of chemistry, and as full as is desirable or possible in a work of this size. But in this division, also, it is to be regretted that the space occupied by pictures and details of manufacturing apparatus and processes was not devoted to medical chemistry.

Part V (94 pp.) contains the analytical portion. The reac-

tions of bases and acids are given with conveniently arranged tabular schemes of qualitative analysis. There are also a few examples of quantitative methods, and descriptions of the more important processes of drug assay. The work concludes with an appendix containing useful tables. R. A. WITTHAUS.

JOHN DALTON AND THE RISE OF MODERN CHEMISTRY. BY SIR HENRY E. ROSCOE. New York and London. Macmillan & Co., 66 Fifth Avenue, New York City. Price, \$1.25. pp. 216; 12 mo. Portrait and facsimile. The Century Science Series.

This is an unusually satisfactory book; it is a pleasure to read the biography of one eminent man written by another distinguished in the same branch of knowledge, who appreciates and sympathizes with his subject and his subject's labors.

Materials for a history of John Dalton and his contributions to chemistry were not lacking. W. C. Henry's "Memoirs" (1854), R. A. Smith's "M memoir and History of the Atomic Theory" (1856), Charles Clay's "Reminiscences" (1884), and Lonsdale's "Worthies of Cumberland" (1874), supply the necessary details of the uneventful, quiet life of the Manchester schoolmaster, and accounts of his momentous researches in chemical philosophy. Besides these sources of information, Sir Henry could refer to his own lecture delivered in the Town Hall, Manchester, in 1874. In this volume we find a summary of Dalton's parentage, school days, and teachers, his experience as a school teacher when only twelve years of age, his first attempts at scientific investigation (meteorological), his connection with the Manchester College, and his pains-taking researches on the relative weights of ultimate particles. The text is pleasantly anecdotal, clearly describing Dalton's personality. The volume is illustrated with a portrait of Dalton, facsimiles of letter and leaflet containing the atomic symbols. One remark of Sir Henry's greatly surprises us; speaking of decimal fractions he says they are "a snare and a stumbling-block even to some great men of the present day." Can it be that calculations in  $\text{£}$ ,  $s$ , and  $d$ . are so deeply impressed on the British mind that they prevent comprehension of decimals familiar to every American school-boy? The book contains an excellent index.

H. CARRINGTON BOLTON.



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## DR. GIDEON E. MOORE.

Received May 31, 1895.

THE death of Dr. Moore happened on Saturday, April 13, 1895. On the following day the death of Prof. James D. Dana was announced. The occurrence so closely together of these sad events was a striking one, for it was under the guidance of Prof. Dana that Dr. Moore entered upon a field of study which he cultivated with so much ardor that his reputation for deep scientific work was increased; and we may well believe that, had not the accidents of fate and fortune turned Dr. Moore's steps from academic halls he, also, would have left the impress of his good and strong personality upon the mind and life of many a youthful student of science.

Gideon Emmet Moore, son of George H. and E. L. Moore, was born in New York City, August 21, 1842. His maternal grandfather, after whom he was named, was Dr. Gideon Humphrey, one of the leading physicians of Philadelphia in the beginning of this century, who distinguished himself as a surgeon in the war of 1812, and took part with remarkable adventures in the filibustering expeditions of the period. His father, whose family belonged in Maine, early went to California, in fact was one of the first settlers of San Francisco, as he was there eleven years before the Argonauts of '49. He embarked in the business of shipping and warehousing, and his firm was the foremost one of the time.

Young Gideon Moore's early days were spent, some in New York and some in Burlington, N. J., and, before entering Yale College, at Dr. Bartlett's Academy in Poughkeepsie. In his boyhood he was passionately fond of music and an accomplished performer on the violin. His class at Yale was '61. Prof. S. W. Johnson has kindly sent me the following tribute to his pupil:

"Our friend, Gideon E. Moore, entered the Yale Scientific School in the Autumn of 1859, graduated as Bachelor of Philosophy in the Summer of 1861, and remained as a postgraduate student until the Spring of 1862.

"During the first year of his attendance I knew him slightly, but from September 1860 until he finished his studies I had immediate charge of the Laboratory of Analytical Chemistry and was constantly familiar with his progress in chemical study. I was from the outset attracted by the gentle and courteous manners of the somewhat delicate appearing youth whose invariable cheerfulness, promptitude, and steady attention to work, no less than the ease with which he performed and exceeded the tasks assigned him, made the duty of his teacher a pleasure and a privilege.

"Having gone through an extended course of inorganic analysis with unusual rapidity and success he was well prepared to take up organic chemistry, and the proposal was made to him (I think in Sept. 1861) to undertake an investigation of Bayberry Wax.

"This research was foreseen to require a long time and to involve much tedious labor, but he entered upon it without hesitation, pursued it steadily for four months, and evidently enjoyed it heartily to the end.

"The results are embodied in his paper—'On the Chemical Constitution of the Wax of the *Myrica Cerifera*'—which appeared in the American Journal of Science, May, 1862. This short paper, of seven pages, presents a concise history of the chemical work previously done on the bayberry wax and established its nature as a mixture of about one-fifth part of tripalmitin and four-fifths nearly of palmitic acid with a little laurin or lauric acid. It illustrates the thoroughness which characterized his work and which made him so immediately successful when, soon after completing his studies at New Haven he engaged in the practice of analytical chemistry at San Francisco, and later when he became assayer to the Gould and Currie mine at Virginia City.

"As I write these lines there stands near by a series of twenty little bottles containing specimens of the fruit, foliage and wax of the bayberry and the preparations obtained during the research in question illustrating the method followed and showing the results arrived at. This instructive collection has done duty regularly for thirty-two years in my lectures and recalls vividly to my remembrance the busy days when our friend was diligently disciplining to extraordinary skill the hand that but a few hours ago suddenly forgot its cunning."

Yours very truly,

S. W. JOHNSON.

Dr. Moore's life in the West was hard enough to daunt the most courageous but he viewed it as a necessary step in his

progress. The rough life of the mining camp and the hardships of that primitive era had no terrors for him. The very task itself of keeping a foothold in such a community only spurred him to accomplish what he had set out to perform, just as in his college and professional career to suggest that a matter was difficult, was sufficient to fire his ambition to attack it and his confidence that he would overcome it.

After four years spent in this field, enjoying in the highest degree the confidence of the owners of the millions which passed through his hands, he resigned to embrace with enthusiasm the opportunity to secure what he had so long coveted—a thorough course at the German universities.

In 1867 he sailed for Europe and studied one year at Wiesbaden under Fresenius. He next went to Heidelberg and under Bunsen, Kirchhoff, Helmholtz, Blum, Vonderden, and Kopp he passed some of the happiest days of his life and was graduated *summa cum laude*. At Leipzig he studied under Kolbe one semester, and at Berlin in the laboratory of Wichelhaus.

In September, 1871, he married in Buda Pest, Marie Louise Von Hildebrandt, the daughter of Field Marshal Von Hildebrandt, of the Austrian army, and in the following month returned to America.

In 1872 he became chemist to the Passaic Zinc Co., and continued in that capacity to the close of his life. The remainder of his time was devoted to study and private practice, a field in which he rose to eminence and left a record marked with many triumphs.

Depth, care, thoroughness, and method characterized his work. His intellectual endowment was generous, his mental faculties keen, his memory good, his power of concentration wonderful. He possessed a logical and well-balanced mind not easily led to hasty conclusions. The virtue of strict, unwavering conscientiousness and fidelity to truth was a shining one in Dr. Moore, and his professional honor was not a mantle to be put on and off or to be distinguished from his personal honor. All his early training as well as the promptings of his heart fortified him in the practice of making diligent search for the truth, and having found it, of fighting bravely for his convictions.

He at one time wrote much and all of it was valuable; in the early days making many contributions to mineral chemistry; Brushite, Cryptocallite and Hetaerolite being additions made by him to the list of new species. Of late years his most laborious work, that on the "Chemistry of American Tobaccos," was written for the Tenth Census. He was editor of Vol. II of this JOURNAL, and in Vol. I appeared his report on the Progress of Analytical Chemistry for 1879—a model for all of its kind. He had taken out many patents in metallurgical and fuel-gas processes.

Subjoined is a list of his published papers:

1862. On the Chemical Constitution of the Wax of the *Myrica Cerifera*. American Journal of Science, [2], 33, 313.

1865. On Brushite, a new mineral species. American Journal of Science, [2], 39, 43.

1866. Analysis of the Water of Borax Lake, Cal. American Journal of Science, [2], 41, 255.

1870. On the occurrence of Amorphous Mercuric Sulphide (*Metacinnabarite*) in Nature. J. prakt. Chem., [2], 2, 319. American Journal of Science [3] 3, 36.

1871. On the Electrolysis of the Substituted Derivatives of Acetic Acid. Ber. d. chem. Ges., 4.

1875. On Chalcophanite, a new mineral species. American Chemist, July, 1875.

1877. On Hetaerolite, a new mineral species. American Journal of Science, [3] 14, 423.

1878. Report on the Strong System of Water-gas Manufacture. Engineering and Mining Journal, January, 1878.

1879. Report on the Progress of Analytical Chemistry, from April to September. J. Am. Chem. Soc., 1.

1883. Report on the Chemistry of American Tobaccos. Special Report of the United States Census, On the Culture and Curing of Tobacco. Chap. 22.

1885. Report on the Granger Water Gas. A. O. Granger & Co., Philadelphia.

1885. Kallait, pseudomorph of Apatite from California. In collaboration with V. von Zepharovich. Ztschr. für Krystallographie, Leipzig.

Dr. Moore's manners were gentle and courteous in the extreme. He used to tell with much appreciation how, when he was working in Bunsen's laboratory, he would always have to keep his eyes averted from Bunsen, who would immediately spring to his side were he to show the slightest sign of effort over the task or

the need of anything. And listening to him telling this you could not help thinking how marked was the same kindliness in himself. How grateful is association with such men. What a privilege to have daily converse with one whose soul delights in those little amenities which the throng overlook. What a pleasure in the cheery face. What a lesson we learn from the lips that may be quivering with pain, but open only to express solicitude for our welfare and to smile that they may hide their own story.

An acquisition that was of great value to our friend was his retentive memory. Everything that he had once mastered, whether in science or in other branches of knowledge, could be recalled to mind at will and with an accuracy and fidelity to detail that made us marvel. I remember on one occasion when in a leisure hour we were discussing the poets, and Coleridge became the subject of our remarks, he recited without hesitation the lines in *Kubla Khan*:

"But oh that deep romantic chasm which slanted  
Down the green hill atwart a cedarn cover!  
A savage place! as holy and enchanted  
As e'er beneath a waning moon was haunted  
By woman wailing for her demon lover!"

I said "You have been reading Coleridge lately?" "No," said he, "I don't suppose that I have read these lines in over twenty years, but I remembered them for I always admired their sonorousness and picturesque effect."

He was a poet himself of no mean order. His nature was essentially grave, retired and full of self-repression, yet it had that expanding joyousness which goes in search of the delights that we may draw from elevated themes and roseate imagery. He had translated much from Goethe, and more recently Hamerling, in lines which show alike his skill as a linguist and his art as a poet.

His end came suddenly, for he was stricken without warning, and he laid down his work to go and face the terrors of pneumonia. He did face them, and unflinchingly, and he calmly awaited the end, that he saw must come, with the fortitude of the Christian faith that he was glad to acknowledge.

CHAS. F. McKENNA.

I spent last Saturday with Prof. T. E. Thorpe in his steam launch on the Thames at Kingston with a party of friends. He asked me then about Dr. Moore's death and spoke of him very warmly. They were students together in Germany and the friendship then formed was cemented by meetings during Thorpe's visit to America afterwards. He detailed at length, incidents of Dr. Moore's student and family life illustrating his lovable character.

Proof of Mr. McKenna's notice came to me in London, and I have ventured to add this note to show that his and Professor Johnson's words find an echo abroad.

EDWARD HART.

London, June 22, 1895.

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### LOTHAR VON MEYER.

BY the sudden death of Lothar von Meyer, which occurred at Tübingen, on April 11th, chemical science has lost one of its foremost exponents.

It was vacation time in Tübingen, and Professor Meyer had returned from a walk and was engaged in his favorite outdoor pastime of trimming vines in his garden when he suddenly began to feel unwell and hastened to his study. He called for help and his wife and son went to his aid. Reaching a sofa with their support he remarked, "I have received a stroke," and then was able to say no more. This was at about 5 in the afternoon, and at 11 he died, without further struggle, his face retaining the calm and noble expression not to be forgotten by his many friends.

Julius Lothar Meyer was born August 19th, 1830, at Varel in the Grand Duchy of Oldenburg, the son of a well-known physician, Dr. August Meyer. He completed his gymnasium course in Oldenburg and began the study of medicine in Zürich in the Spring of 1851. There he spent four semesters, followed by two semesters at Würzburg, where he received the degree of Doctor of Medicine, in the Spring of 1854, for a thesis on the question of the condition of gaseous combinations in the blood. In the investigation of this problem Meyer's attention was attracted to the recent work of Bunsen on gas measurements, and accordingly we find him next in Heidelberg, where he re-

mained five semesters, at a time and in a company since famous in the history of chemistry. He took up again the question of the gases held by the blood, and in a long investigation, published in 1857, he showed for the first time the real nature of the oxygen absorption. Magnus had shown at an earlier date that the oxygen absorbed by blood did not follow the Dalton-Henry law, but he attempted no explanation for this fact. It remained for Meyer to determine the quantity of oxygen, carbon dioxide, and nitrogen absorbed under different conditions, and to show that the absorption of the first must depend on chemical combination. This investigation attracted immediate attention.

Meyer's tastes now led him away from medicine and in the direction of pure chemistry, and especially toward physical chemistry. Leaving Bunsen, he went to the old university of Königsberg, attracted by the courses of lectures given by Franz Neumann on the subject of mathematical physics. He remained with Neumann three semesters. In the Spring of 1858 Meyer went to Breslau, where he was given the degree of Doctor of Philosophy for a dissertation on the absorption of carbon monoxide by the blood. In this dissertation it was shown, for the first time, that CO displaces O, volume for volume. The author soon afterwards became a *Privatdocent* for physics and chemistry, and, in 1859, was given the position of Director of the Chemical Laboratory of the Physiological Institute. Here he remained until 1866. In this interval he published a number of valuable papers, and the first edition of his famous work, "Die modernen Theorien der Chemie."

In 1866 he was called to the Forestry Academy of Eberswalde, in 1868 to the Polytechnicum of Karlsruhe, and in 1876 to the University of Tübingen, where he had just completed his nineteenth year of labor at the time of his death.

Lothar Meyer was the author of numerous valuable scientific papers, most of which appeared in *Liebig's Annalen* and in the *Berichte*. They handle mainly questions from the field of physical chemistry. In some of his earlier papers Meyer began the study of the relations existing between the atomic weights and physical and chemical properties of the elements. Their relations were soon formulated in his Periodic System of the Elements.

That Mendelejeff arrived independently at almost the same conclusions does not, in any measure, detract from the originality or value of Meyer's work. It is this work which has made his name best known among scientific men, but without it his purely experimental investigations would be sufficient to give him a high position among the great chemists of the time.

In recognition of his services to science, Meyer received the Davy medal of the Royal Society in 1882, was made a Foreign Honorary Member of the London Chemical Society, in 1883, Corresponding Member of the Prussian Academy of Sciences, in 1888, and in 1891 a Corresponding Member of the Russian Academy. In 1892 he was given a title of nobility by decree of the Würtemberg crown.

He was the author of the following works: "*Die modernen Theorien der Chemie*," first edition 1864, fifth edition 1884, a sixth edition the author had in preparation; "*Die Atomgewichte der Elemente*" (with Karl Seubert), 1883; "*Grundzüge der theoretischen Chemie*," first edition 1890, second edition 1893. The first and last of these books are well known in English translations.

It is not necessary, in this place, to speak of the high scientific value of Meyer's work, as that is a subject on which the literature itself speaks most plainly. He possessed great manual dexterity, and in glass-blowing and the construction of apparatus he had unusual skill. His style, as a lecturer, was simple and exceedingly clear, and in his everyday intercourse with students he displayed a kindliness of disposition and patience in explanation not often found with men whose time is as closely occupied as was his. Few investigators are willing to give from their private work the time which he freely gave to interested students.

Among his colleagues Meyer was cordially respected and beloved. Last summer he was appointed Rector of the University for the present year, and by other distinctions, as well, his popularity was shown. All who knew him mourn his loss as a man; chemists alone are able to recognize the loss to science.

J. H. LONG.

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### THE CHEMICAL HISTORY OF A CASE OF COMBINED ANTIMONIAL AND ARSENICAL POISONING.<sup>1</sup>

BY CHARLES A. DOREMUS, M.D., PH.D.

Received May 17, 1895.

THE coffin plate disclosed on opening the outer box of rough wood, bore the inscription, "Gustave H. M. J. Baum, died March 30th, 1892. Aged 26 years, 3 months, and 4 days." It was untarnished and affixed to a black cloth-covered casket. The condition, not only of the outer and that of the inner case, but also that of the lining of the latter and of the clothes about the body excluded the possibility of there having been any infiltration of liquid from the grave and rendered the examination of any soil from the cemetery superfluous.

The emaciated body of a medium sized man was identified by the physician who had attended him in life and verified his death and by the undertaker and his assistant who had prepared the body for burial.

Though three months had elapsed since the interment, it was possible on July 6th, 1892, to recognize the features, also an abrasion on the right shin. There was some mould about the face and body, the latter being disclosed when the clothing was removed. The features of the corpse bore a marked resemblance to a photograph of a man named Ludwig Brandt.

Both Baum and Brandt had been quondam acquaintances of a Dr. Henry Meyer. Insurance had been secured on the life of

<sup>1</sup>Read at the May Meeting of the New York Section.

Baum in four companies, amounting in all to \$8,500. Brandt had personated Baum in making application for these policies, had come to New York in company with Dr. Meyer, a woman posing sometimes as Mrs. Meyer, at other times as Mrs. Baum, and one Mueller.

After the death of Brandt the woman applied to the different insurance companies for the sums due, representing herself as his widow. Several of the companies paid in full, a total of \$4,000.

Accompanied by Dr. Meyer she visited the offices of the Mutual Life Insurance Co., of New York. The interview aroused suspicions which were subsequently increased by the sudden disappearance from New York of the parties, their effects having been sold and no word being left of their destination.

At the instigation of Mr. Daniel Gillette, of the Mutual Life Insurance Company, detectives were sent in search of the parties with the view of unearthing any crime that might have been committed. Mr. H. G. Julian, acting in this capacity, had been able to secure a description of the supposed Baum, and found the body to agree not with him but with a photograph and description of Brandt.

Dr. L. W. Schultze, one of the coroners of the city, deemed this initial evidence of sufficient weight to order an autopsy and conducted it with his medical assistants. Dr. S. P. Minden, who identified the body, had attended the man for three weeks before his death, and gave a death certificate ascribing the demise to chronic dysentery. He had not noticed any unusual circumstances during this attendance. Had not Dr. Meyer borne an unenviable reputation, it is probable that no further notice would have been taken of the case; but because of his career extra caution was taken at the autopsy to determine, if possible, if the pathological condition agreed with the diagnosis of the physician.

The surface of the body was carefully scrutinized. There were no marks of hypodermic injections, however, nor any evidence of embalming by arterial or other injections. The undertaker declared that no attempt was made to embalm the body and that no embalming fluid was used upon it or injected into

it. Three channels for the introduction of poison; *viz.*, imbibition from the soil, the use of embalming liquids, and the use of hypodermics were thus eliminated. Coroner's physician, Dr. O'Hare, and Prof. D. Hunter McAlpin, who at a subsequent time examined the viscera with Dr. O'Hare, could find no gross or microscopic pathological evidence of importance, so that full light as to the cause of death was not obtainable from the autopsy. At the autopsy Dr. S. P. Minden related the symptoms he noticed during his attendance on the patient. They did not develop any theory of death other than dysentery, but left the case still obscure. Later he kindly furnished copies of the prescriptions he had written. At the trial, testimony was given to show that some of these prescriptions had been filled but there was no evidence that the medicines had been administered. However, since remedies such as morphine, opium, copper arsenite, and bismuth subnitrate had been prescribed, it became necessary to consider them in any scheme of chemical analysis. The advisability of a chemical analysis was discussed and decided on as necessary to fully determine the cause of death. There was every probability that great skill had been used in the administration of any toxic agent or that some unusual poison had been employed.

Though due care was exercised at the autopsy to detect the odor of any volatile poison none was perceptible and there were no circumstances that in any way directed attention to that class of poisons. The analysis proper, therefore, was begun with the treatment of portions of the viscera for the alkaloids. For this purpose the stomach and its contents, one half of the intestine and its contents, and one-half of the liver, and some fluid which had exuded from it into the abdominal cavity at the time of the autopsy, were treated.

Freshly rectified alcohol was placed on each separate part, 500, 600, and 800 cc. being used respectively. The organs were comminuted and the alcohol acidulated with tartaric acid. The jars remained in an ice chest until a thorough maceration was effected. The alcohol and washings with alcohol was filtered from the tissue and the undissolved substances, which latter were utilized for the detection of inorganic poisons, as were also such other

residues from the extraction as could be utilized for this purpose.

The necessity for doing this is not generally recognized. Some of the salts of the metallic poisons are quite soluble in the menstrua employed in extracting the alkaloids and pass into solution with the latter. Previous cases had shown this, one which the writer examined as associate expert, involving the detection of morphine in an embalmed body, very markedly.<sup>1</sup>

In this latter instance, it was of paramount importance that the arsenic extracted in large quantities from the viscera should be separated from the trace of morphine that might coexist, and a prolonged series of extractions was resorted to to eliminate the possibility of mistaking the reactions of the one for the other. This procedure was also necessary to anticipate what was subsequently brought forward by the defence, *vis.*, a point raised by Otto.<sup>2</sup>

The production of arsines and other metallo-organic compounds must also not be lost sight of, for both in testing for organic and inorganic poisons, these exceptionally interesting compounds have been and are likely to be important objects of toxicological research. The fact that evidence of metallic poisons is obtainable from the extractions practised to separate the alkaloids must always be borne in mind, no matter whether the Stas, Erdmann-Uslar or Dragendorff method is employed, or some modification of them, as also when dialysis is resorted to.

Such a course is especially necessary in cases where, in order to recover the very minute quantity of alkaloid that may still remain in a stomach or intestine, the whole of either organ and its contents is submitted to processes for its recovery. Failure to detect an alkaloid may with these precautions in some cases be followed by the finding of an inorganic poison.

It is doubtful whether the method prescribed in many foreign countries, and followed in the laboratory of toxicology in Paris,<sup>3</sup> of comminuting each organ and then mixing together weighed portions of each and of submitting the composite mass to analysis is altogether a wise or safe proceeding. Our own experience is much against it.

<sup>1</sup> People vs. Robt. W. Buchanan, 1600.

<sup>2</sup> Otto: *Ausmittlung der Gifte*, 1884, 117.

<sup>3</sup> Documents du Laboratoire de Toxicologie, Paris, 1891, 23.

The chances of detecting any alkaloid are greatly reduced and the same can be said of metallic poisons. The unequal distribution of poisons through the viscera, and the retention of poisons in certain organs in preference to others, are two of many reasons why a mixture of a fourth of several, say, stomach, intestine, liver, brain, and kidneys, is inadvisable. Nor can there be any hard and fast rule laid down to apply to all cases in the search of poisons. The judgment of the expert must determine in some measure the method to be pursued, and he will naturally have in mind the facts which have been ascertained heretofore, and which have led to the establishment of rules of procedure.<sup>1</sup> No matter what course is followed, it will sometimes happen that important data in regard to the distribution or absorption of the poison detected are unobtainable which could have been secured had the nature of the poison been manifested in the symptoms or indicated by the history of the case. Where, therefore, prominent symptoms are developed, or the autopsy reveals the character of the poison, even if only to so slight an extent as to indicate whether organic or inorganic, narcotic or corrosive, it may best subserve the ends of justice to examine the contents of the stomach apart from the tissue, the gall-bladder and its contents separately from the liver. The fluids of the intestinal tract and the compacted feces near the rectum separately from each other and the tissue. Much will depend in adopting a course as elaborate as this upon the time that has elapsed since death. A long interment would obliterate to a great degree the clearness of the picture of the distribution of the poison in the body, which we might expect to have developed.

While recent analytical results have tended to show that poisons rapidly diffuse in the body, either when injected post-mortem or imbibed by application to the skin, or though taken in life have afterwards permeated the tissues and reached other organs, we take issue with the claim advanced by the defense in this trial, that toxicology is utterly unable to-day to decide whether a poison extracted from the body has or has not been administered before death.

Though weighable quantities of copper were obtained from the

<sup>1</sup> Dragendorff *Ermittlung von Giften*, 4, 1884.

liver and brain in the case now before us, only traces were found in other organs and in some none at all. Such facts are inexplicable on the basis of post-mortem diffusion. It is therefore of great moment to determine more closely not only the localization of a poison but how intimately it is combined with the tissue. A simple permeation may have taken place, or a definite union or fixation, and such union would often be indicative of vital processes. The employment of suitable solvents will thus lead us to a diagnosis between such true chemical compounds and mere loose impregnations. Tissues are found by the dyer to absorb only certain dyes though they may be transiently stained with others. When in contact with poisons, certain living tissues "dye in the wool."

The alcoholic extracts of stomach, intestines, and liver, were evaporated each by itself and each residue thus obtained treated with strong alcohol and filtered. The new alcoholic extracts now of small volume were again evaporated and their aqueous solutions while still acid treated successively with petroleum ether, benzene, and amyl alcohol. All of these liquids had been especially rectified. After the last amyl alcohol extraction was effected several fresh shakings with petroleum ether were resorted to to remove amyl alcohol from the watery liquid. The aqueous solution was then made alkaline by ammonium hydroxide, and the extractions with petroleum ether and benzene conducted as before. The solution was then acidified, hot amyl alcohol added and emulsified, then enough ammonium hydroxide added to render the solution alkaline. This procedure was repeated often enough to make sure of the extraction of any morphin. Six residues were thus obtained from each of the three viscera. It was a noticeable feature of this case compared to two other investigations made just previously that the residues were of less quantity than in either of the other cases, and that many were indeed so insignificant as to be incapable of purification. Residues I, II and IV were very slight or inappreciable.

Of course, residues VI, from the alkaline liquid extracted by amyl alcohol were submitted to the closest scrutiny. Not only had morphin been prescribed, but it was desirable to ascertain if the ptomaines present might either give or mask the morphin

reactions. After suitable purification they were tested. The morphin reactions were not obtainable, some of the ptomain reactions were pronounced. Minute quantities of morphin solution added to portions of the residues could be detected by appropriate tests. The physiological test of morphin applied to a frog was not obtained. Neither morphin nor other poisonous alkaloid could be identified in any of the residues.

The inorganic poisons claimed attention next. Small quantities of copper arsenite had been prescribed; bismuth also as subnitrate. These metals might therefore be present.

The comminuted tissues, subsequently residues from parts treated for organic poisons, were disintegrated by hydrochloric acid and potassium chlorate. Fresenius and von Babo's method was applied to the stomach first and the results obtained showed the necessity of using the same process with the other organs. A copious precipitate formed the moment hydrogen sulphide was conducted into the faintly acid liquid which had been previously deprived of chlorine by bubbling carbon dioxide through it. The color of the precipitates thus obtained varied with the different organs, but was evidently metallic and not of organic nature. The precaution was taken in the analysis of each separate organ to subject the liquid after saturating it with hydrogen sulphide to warmth and long standing to effect a complete precipitation of the metals.

The precipitates were collected, redissolved in small quantities of hydrochloric acid and potassium chlorate and reprecipitated with previous precautions.

The purified sulphides were washed free of chlorides by dilute hydrogen sulphide water and a separation of the different metals attempted.

It will shorten the story considerably to state that mercury, lead, bismuth, and tin were not detectable in any organ. That zinc was tested for carefully in the filtrate from the hydrogen sulphide and not found.

That antimony and arsenic and in some organs these and copper were separated and identified.

Ammonium sulphide was found to dissolve the washed precipitate entirely or to leave only a small amount of copper sul-

phide. This solution was evaporated and oxidized by nitric acid. Then fused with sodium carbonate and sodium nitrate. When copper was present a dark mass separated. In other cases a white powder was suspended in a clear liquid and all became a white solid on cooling.

At this juncture one of the greatest obstacles was met.

Otto<sup>1</sup> would have us believe that the separation of antimony from arsenic by Meyer's method is as facile and as complete as the destruction of organic matter. He enters into a discussion concerning the methods of manipulation and gives a device for still further preventing dissolved antimony from producing a mirror in the Marsh test by conducting the gases evolved over caustic alkali, a very objectionable process as we shall see later, and comes to the conclusion that the method is reliable.

Notwithstanding all this, the history of this analysis shows first, that when very small quantities of antimony are present they would escape notice when the fused mass is dissolved in water and possesses an *alkaline* reaction as required; secondly, that where much antimony is present it is advisable to resubject the insoluble residue to a second fusion to remove possible traces of arsenic.

The finding of antimony and arsenic in the first organ analyzed, naturally put us on our guard in the testing of others.

Where much antimony was found, there was of course an insoluble white residue, but the brain and muscle contained so little that only the most painstaking work enabled us to detect the antimony and separate it from the arsenic. Since some antimony remains in the Marsh apparatus, the whole not passing out as hydrogen antimonide undiscovered pyroantimoniate may go into solution when the fused mass is dissolved in water and either produce a mirror with arsenic or remain in the generator.<sup>2</sup>

The fact that all the antimony is not converted into gas in the Marsh process renders the use of Hofmann's silver nitrate method unserviceable for the quantitative separation and estimation of antimony and arsenic in toxicological analysis.

While all things considered Meyer's method seems the best

<sup>1</sup> Otto, op. cit., 164.

<sup>2</sup> Dragendorff *Ermittlung der Giften*, Dritte Auflage, 406, 1888.



available, the experiences of this case justify us in cautioning against a too implicit reliance upon it.

The finding of antimony in the stomach was followed by detecting arsenic also. The other organs also revealed the presence of each.

In three viscera, copper was noticeable. The liver yielded 0.0056 gram, the brain and muscle, traces.

The entire quantity of copper extracted from the liver was converted by a small portion of the arsenic obtained from the same organ into copper arsenite and presented as an exhibit along with other portions of the arsenic, there being a great excess of the latter. The absence of copper from the stomach and intestines and its disproportion to the arsenic in the liver and the quantity of each poison found seemed sufficient proof to decide in the negative the question of the copper arsenite prescribed being the source of the arsenic found. Since the copper when found had passed together with antimony and arsenic into the ammonium sulphide solution, then to the fusion, it remained undissolved with the pyroantimoniate and had to be separated from the antimony. This operation followed the incineration of the filters, and their contents of sodium pyroantimoniate, in either very small crucibles or porcelain dishes and the fusion of the residues with potassium cyanide. In the case of the intestine the filter was not very small since a considerable amount of sodium pyroantimoniate had been separated. The contents of the filter were removed to a capsule and the filter incinerated. A slight amount of char was left. A drop or two of nitric acid was put on this and heat applied to expel all acid. Whether this was not effectual or some trace of sodium nitrate remained undecomposed is uncertain, but sufficient was left to cause a sharp explosion when the fusion with potassium cyanide was quite well under way, projecting most of the unfused mass out of the dish. While the presence of antimony in large quantity in the intestinal tract was still clearly demonstrated from the residue left in the dish, a quantitative determination of the whole was out of the question. Otto alludes to the possibility of such an explosion in connection with Fresenius and von Babo's method of obtaining arsenic by reduction with potassium cyan-

ide and sodium carbonate, and very naively says "Mir ist bei sorgfaeltigem Arbeiten nie Derartiges vorgekommen."

Although great care was exercised, the accident did happen in the above instance and though the filter ash of the antimonial precipitates from other viscera were in one or two cases similarly treated without the slightest trouble, we caution against the use of nitric acid or an insufficient washing of the pyroantimoniate.

Antimony was weighed either as metal in powder or on platinum, as sulphide or as tetroxide,  $\text{Sb}_2\text{O}_3$ .

Arsenic was weighed either as mirror obtained by the Marsh test or as sulphide. Two mirrors of arsenic were estimated baroscopically.

Organ.	Weight in grams.	Antimony weighed as grams.	Antimony calculated to grams.	Antimony calculated as tartar emetic.
Stomach and contents....	130	Sb 0.0307	0.03070	0.08404
Intestines and contents } .	898	Sb 0.0042		
	47	$\text{Sb}_2\text{S}_3$ 0.0072	0.00936	0.02562
Liver, spleen, and fluid } ..	988			
from abdomen. }	?	$\text{Sb}_2\text{O}_3$ 0.1442	0.11423	0.31314
Heart .....	224	$\text{Sb}_2\text{O}_3$ 0.0028	0.00221	0.00605
Kidneys .....	315	.....	.....	.....
Brain .....	820	$\text{Sb}_2\text{O}_3$ 0.0003	0.000237	0.00065
Muscle .....	227	$\text{Sb}_2\text{O}_3$ 0.0004	0.000317	0.00086
			0.157054	0.43036
			equivalent to 6.64 grains.	

Organ.	Weight in grams.	Arsenic weighed as grams.	Arsenic calculated to As.	Arsenic calculated to As <sub>2</sub> O <sub>3</sub> .
Stomach and contents....	130	As <sub>2</sub> S <sub>3</sub> 0.0063	0.00384	0.00507
Intestines and contents } .	898	As <sub>2</sub> S <sub>3</sub> 0.1888	0.11512	0.15196
Liver, spleen, and fluid } .	47			
from abdomen }	988	As <sub>2</sub> S <sub>3</sub> 0.1134	0.06914	0.09127
Heart .....	224	As 0.0003	0.00030	0.000396
Kidneys .....	315	As 0.0580	0.05800	0.07656
Brain .....	820	As 0.0002	0.00020	0.000264
Muscle .....	227	estimated.		
		0.0001	0.00010	0.000132
		estimated.		
			0.24670	0.325652
			equivalent to 5.02 grains.	

It was deemed important to produce evidence before the jury to confirm the statement that both antimony and arsenic existed in the viscera of the body exhumed. To this end the antimonial and arsenical compounds isolated from the several viscera were brought into weighable form. After weighing, these compounds were submitted to special tests, the results of which in many in-

stances were reserved as *corpora delicti*. These consisted in the case of

*The Stomach* of antimony as metal from the cyanide fusion ; antimony on platinum and on tin ; the oxide and the sulphide.

Bunsen tests, metal, sulphide, and reaction of oxide with silver nitrate and ammonia.

The arsenic was shown as a mirror obtained by Fresenius and von Babo's method. (No antimony could be detected in the fused mass of cyanide.) Arsenious sulphide and silver arsenate were also presented as exhibits.

*The Intestine.* Antimony was shown as metal on platinum and as sulphide ; arsenic as Marsh test mirror and oxide ; also the resulting mirror of a Marsh test using electrolysis ; further, a Reinsch deposit on copper and a sublimate of arsenious oxide therefrom ; silver arsenite, copper arsenite, arsenious sulphide, silver arsenate, magnesium ammonium arsenate and Bettendorff's test with stannous chloride.

*The Liver, Spleen, and Fluid.*—Antimony was shown by Marsh test, metal, silver antimonide and oxide ; deposit from hydrogen antimonide on potassium hydroxide ; antimonious sulphide, antimonie oxide, antimonious oxychloride, the metal on platinum and on tin ; Bunsen's flame tests, metal and sulphide ; Reinsch's test, metal and sublimate.

Arsenic, by Marsh test, elementary and oxide ; deposit made from passing hydrogen arsenide over potassium hydroxide ; silver and copper arsenates.

*The Heart and Blood.*—Antimony was shown as metal and sulphide ; arsenic, as Marsh mirror.

*The Brain.*—Antimony was shown as sulphide ; arsenic, as Marsh mirror.

*The Muscle.*—Antimony was shown as sulphide ; arsenic, as Marsh mirror.

The Marsh test was conducted with the usual precautions and using zinc, slightly platinized, and sulphuric acids of varying strengths.

The apparatus was modeled after that proposed by Prof. R. Ogden Doremus, in 1859, and used in the trial of *The People vs. James Stephens*, since which date no other case of criminal poisoning by arsenic has been tried in New York City, until the

one now under consideration. At a subsequent date, 1878, the same observer, made another change during an investigation of a case where attempt to poison by antimony was charged, *viz.*, The People of the State of New Jersey vs. Rev. Geo. B. Vosburgh. Dragendorff's statement of the decomposability of hydrogen antimonide by stick potassium hydroxide was then verified, but his other statement that hydrogen arsenide does not undergo change was then disproved. This observation has been corroborated by Johnson and Chittenden<sup>1</sup> and in this case.

Dragendorff,<sup>2</sup> in his fourth edition which has just come to hand, modifies his statement concerning the decomposability of hydrogen arsenide by stick potassium hydroxide and refers to work done by Kühn and Säger in this connection. The quotation in the footnote shows that they were anticipated in this matter by R. Ogden Doremus.

Repeated experiments with various kinds of stick sodium and potassium hydroxides have been made since 1878, and though the darkening by arsenic is not as pronounced as with antimony, there is abundant evidence of it. The stains fade more readily. To avoid the loss of arsenic therefore, it has been customary with us to use fragments of pure caustic lime as a drying agent. These at least show no outward sign of a decomposition of either hydrogen antimonide or arsenide.

A small Erlenmeyer flask, well cooled and having granulated zinc within, had acid and when purged of air acid and suspected liquid fed into it from a stop-cock funnel. The escaping gas was dried by a layer of quick-lime between cotton plugs, and then conducted through several inches of hard glass tubing coiled in a spiral, surrounded by a hood and heated by a strong Bunsen flame. The escaping gas was conducted into a solution of silver nitrate.

A complete decomposition of the hydrogen arsenide occurs, no mirror appearing on a second coil, which may be added for precaution. Some of the Marsh tests were conducted with the view of weighing the mirrors, which was done except with the brain

<sup>1</sup> Dragendorff, *op. cit.*, 406; Otto, *op. cit.*, 198; Fresenius' System of Quantitative Chemical Analysis; Am. Ed. 1881, p. 782. "Otto and also Dragendorff recommend to pass the gas first over fragments of caustic potassa. We find, however, in accordance with Doremus, that arsenic is arrested by caustic alkali. S. W. J. and R. H. C."

<sup>2</sup> Dragendorff Ermittlung von Giften, vierte Auflage, 386 and 410.

and muscle, where they are so small as to render their retention as exhibits of greater importance than the ascertaining of their weight.

In other cases the Marsh test was used as a proof of the assertion that antimony and arsenic had been isolated. This last was particularly the case in the liver tissue, from which considerable quantities of each poison had been separated. A potassium hydroxide tube was therefore inserted instead of the quicklime, and well-defined black deposits obtained not only on the hydroxide but by the heated coil with antimony and arsenic, the antimonial deposit formed by the action of heat being on the side towards the generator, that of the arsenic beyond the heated spiral.

The arsenical deposit on the hydroxide is therefore of special interest.

Wormley<sup>1</sup> and others lay stress on the fact that the arsenical mirror forms beyond the heated portion of glass.

While conducting a Marsh test by the electrolytic evolution of hydrogen a gradual weakening of the current caused a gradually diminishing flow of gas.

A mirror of the character of those of arsenic formed on each side of the heated spiral. That these were both arsenical was proved by their being soluble in sodium hypochlorite solution, as well as from the extreme care taken to separate antimony from arsenic before employing the latter in the Marsh test.

Antimonious oxide occurs not only as valentinite but as prisms in exetele and as octahedra in senarmontite. The latter resembles ordinary arsenious oxide, a beautiful example of isodimorphism.

Just beyond the hottest part of a spiral employed in making a Marsh test for antimony we observed a crystalline deposit. The crystals were transparent octahedra, did not sublime when the tube was heated, and became red when acted on by hydrochloric acid and then ammonium sulphide. We have therefore apparently an instance of antimonious oxide depositing in the usual octahedral form of arsenious oxide.

Where admissable on account of quantity of arsenic or antimony at our disposal, the gases generated in the Marsh test were

<sup>1</sup> Micro-chemistry of poisons, 229, 1885.

conducted through a silver nitrate solution before heating the spirals.

Though a darkening of the liquid was obtained in each instance, no arsenical reaction could be obtained from the liquid where the suspected antimonial solution was being added to the generator, nor antimony from the black deposit, where a supposably arsenical solution was under test. Antimony and arsenic revealed themselves however in the deposits in the former and in the liquid in the latter, a further evidence that a thorough separation of the two poisons had been effected in the analysis.

The statement is made that selenium hydride yields a black stain to glass at the heated portion, the stain remaining black as long as the glass is hot, but becoming invisible or white in character when the glass cools. We have verified this by experiments made with sulphuric acid containing selenium, a kind of acid not difficult to secure nowadays. Indeed, much sulphuric acid sold as chemically pure should be rejected for toxicological work solely on this ground. This dark stain on the glass is quite distinct from the one alluded to by Wormley<sup>1</sup> as due to arsenic in the glass or to the reddish-brown deposit given by selenium hydride when this gas is tested by the Marsh-Berzelius method. In connection with special tests, we desire to draw attention to the great delicacy of the flame tests when conducted by the methods suggested by Bunsen. We have had occasion to use them in a number of toxicological cases with marked success. In the Vosburgh case many of the exhibits shown were obtained with very small quantities of antimony by these means. Specimens of both antimonial and arsenical reactions were obtained in this investigation and formed part of the exhibit. As a rapid method of bedside testing, these reactions are most excellent. A small sliver of mica is a good substitute for asbestos fiber, and the suspected material can be readily introduced into a small reduction flame of either a Bunsen burner or alcohol lamp, while the oxide tests may be secured with the aid of a candle flame. A bit of china is a good substitute for a capsule, and may be used to catch the deposits by either crushing down the flame or holding it a little distance above it. The deposits may then be tested with suitable reagents.

<sup>1</sup> Wormley. *op. cit.*, 319 and 290.

As an adjunct to the Marsh test for arsenic, when a good-sized mirror had been obtained from a portion of the arsenic, extracted from the intestine, the hydrogen apparatus was removed and dry oxygen obtained by electrolysis was slowly passed in the reverse direction to the hydrogen current. The mirror was then gently heated at the side nearest the coil and the current of oxygen drifted the arsenious oxide formed through the first cold portion beyond where beautiful octahedral crystals were formed.

Although the work thus outlined had been conducted with the assistance of Prof. John A. Mandel, who is jointly entitled to any credit belonging thereto, yet to anticipate certain legal quibbles, the District Attorney, Mr. De Lancey Nicoll deemed it expedient to submit a portion of the viscera for analysis to some one entirely unfamiliar with the history of the case. Prof. R. H. Chittenden was therefore requested to make an independent analysis of the kidneys, which resulted in his finding both antimony and arsenic. The former was in unweighable quantities. The arsenical mirrors obtained from the 315 grams of the kidneys weighed 0.0058 grams.<sup>1</sup> Prof. Chittenden then came to New York and together we analyzed the heart, finding antimony and arsenic as previously stated. The results of his analyses of the kidneys made a separate exhibit which he presented before the jury in his direct examination as a witness.

The defense did not dispute the finding of arsenic and antimony but attempted to show the impossibility of determining whether these poisons had not been introduced by some means after death. The medical history of the case, the condition of the body at the autopsy, the results of the pathological examination, and finally those of the chemical analysis were deemed sufficiently conclusive to the minds of the experts for the prosecution, to make special tests to elucidate this claim uncalled for. No testimony was produced by the defense to show that anyone had so introduced the poisons or had a motive to do so.

During the summing up by the defense, one of the jurors suddenly became insane. It was a recurrence of mental aberration

<sup>1</sup>The entire record of the case will be published under the direction of Assistant District Attorney John E. McIntyre.

which was totally unexpected. He had denied ever having had any mental disease when catechised previous to his acceptance as a juror. A second trial was therefore necessary. It resulted in a verdict of imprisonment for life.

The wife of the prisoner was held in custody for many months, but was finally released on her own recognizance. She had presented herself at the insurance offices dressed in appropriate mourning and claiming to be the widow of "Baum." Several of the companies made payments which she accepted.

It is a noteworthy circumstance that the history of antimonial poisoning is so frequently connected with the destruction of lives heavily insured. Taylor,<sup>1</sup> in a monograph, gives some remarkable cases. In some of these a second poison was administered. Though there have been cases where arsenic has been found along with antimony its presence has been due to the impure nature of the antimony. We have not been able to find the record of any case of chronic antimonial poisoning followed by the use of arsenic as a toxic agent.

BELLEVUE HOSPITAL MEDICAL COLLEGE,  
May 10, 1895.

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[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. No. 4.]

### ACTION OF HYDROCHLORIC ACID GAS UPON SALTS OF THE ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received May 3, 1895.

IN a former number of this Journal (*Vol. XI, 578*) we took occasion to call attention to the rather interesting behavior of sodium vanadate, when gently heated in an atmosphere of hydrochloric acid gas. The results obtained by us proved that vanadic acid is entirely expelled from its salt by this means. This behavior naturally suggested a line of investigation, which we hoped to begin at once, but it was not until very recently that we were able to resume the study. The idea as to whether the salts of the acids of other elements of Group V of the Periodic System were similarly transposed by hydrochloric acid gas, or by the gaseous haloid acids in general, constantly obtruded itself.

<sup>1</sup> On Poisoning by Tartarized Antimony. A. S. Taylor, M.D., F.R.S., Guy's Hospital Reports, Third Series, 3, 369, 1857.



We accordingly turned to sodium nitrate and submitted it to the action of hydrochloric acid gas, aiding the reaction by a gentle heat. The gas was evolved by dropping concentrated sulphuric acid from a funnel tube into commercial hydrochloric acid. From the evolution flask it passed through an empty bottle and then through sulphuric acid, from which it entered a combustion tube carrying a boat containing the salt to be acted upon. The products of the reaction were conducted into water, contained in a bulb-receiver, to which was attached a small Erlenmeyer flask containing water.

When the gas came in contact with pure sodium nitrate, action set in even in the cold. The salt assumed a brown-yellow color and a yellow liquid condensed in the cooler portion of the combustion tube. On the application of heat this was driven into the receiver. The action was continued for fifteen minutes, after which the boat was allowed to cool in the gas and then transferred to a vacuum desiccator, where it remained for an hour before it was weighed. An examination of its contents revealed the presence of nothing but sodium chloride. That the conversion was quantitative is evident from the following data:

*Experiment 1.*—0.1878 gram of carefully dried nitrate gave 0.1289 gram of sodium chloride, while the calculated quantity of the latter is 0.1290 gram.

*Experiment 2.*—0.3536 gram of nitrate gave 0.2429 gram of chloride, instead of the theoretical 0.2428 gram.

*Experiment 3.*—0.2971 gram of nitrate gave 0.2040 gram of chloride, while the required quantity is 0.2041 gram.

*Experiment 4.*—0.6462 gram of nitrate gave 0.4440 gram of chloride, instead of 0.4439 gram, as required by theory.

In experimenting with phosphates we used pure sodium pyrophosphate. We found that this salt was not affected when subjected to the action just described. Nothing was expelled from it. When sodium pyroarsenate was substituted for the phosphate action did occur; the arsenic was completely volatilized and collected in the water contained in the bulb-receiver. The contents of the latter were carefully poured into a beaker glass and oxidized with a few drops of nitric acid. Later a "magnesia mixture" was added to the neutralized solution, which was permit-

ted to stand fifteen hours before the magnesium ammonium arsenate was filtered. It was finally weighed as magnesium pyroarsenate. The contents of the boat were also dissolved and tested for arsenic, but none was found.

*Experiment 1.*—0.3844 gram of sodium pyroarsenate gave 0.3355 gram of magnesium pyroarsenate, instead of 0.3361 gram, the quantity required by theory.

*Experiment 2.*—0.1093 gram of sodium pyroarsenate gave 0.0959 gram of the magnesium salt, instead of 0.0956 gram, the calculated quantity.

In these experiments a colorless liquid collected in the cooler portions of the tube beyond the boat, but this disappeared upon the application of a gentle heat.

In a third trial the aqueous arsenic solution was not oxidized, consequently the arsenic obtained by precipitation with the "magnesia mixture" was far from the required quantity. From this we infer that the arsenic is not volatilized wholly as a derivative of its higher oxide. The latter doubtless suffers partial reduction. We are striving at present to ascertain in what form it is removed. When it is considered that vanadic acid is expelled as an oxychloride, analogy would suggest some similar form for the arsenic. Of this, however, we expect to speak more definitely in the future.

Care should be exercised in heating the sodium pyroarsenate in the hydrochloric acid gas, as the salt when heated in it fuses very readily, and after fusion sets in the acid acts rather slowly. Magnesium pyroarsenate and lead arsenate were found to be converted quite as readily, by the gas, into their chlorides and the arsenic as completely eliminated as in the case of the sodium salt. The corresponding phosphates remained unchanged.

The separation of the two acids, when associated as sodium salts, as magnesium salts, and lead salts, was tried.

*Experiment 1.*—A mixture, consisting of one-tenth gram of sodium pyroarsenate and an equal amount of sodium pyrophosphate, was treated as just described. The arsenic found in the bulb-receiver and weighed as magnesium pyroarsenate, was 0.0869 gram. Theory required 0.0874 gram. The phosphate remaining in the boat was dissolved in water and the acid finally

weighed as magnesium pyrophosphate. It equaled 0.0830 gram instead of 0.0834 gram, the theoretical quantity.

*Experiment 2.*—In this trial 0.1100 gram of each salt was used. The volatilized arsenic, weighed as pyro-salt, equaled 0.0957 gram, instead of 0.0961 gram. The non-volatilized phosphorus, weighed in the same form, equaled 0.0909 gram, instead of the theoretical 0.0918 gram.

We next prepared magnesium pyroarsenate and magnesium pyrophosphate. Mixtures of these salts were then acted upon by the acid gas. Two separations were made with the following results:

*Experiment 1.*—0.1100 gram of each salt brought into a boat was acted upon by the acid. No difference from the behavior of the sodium salts was observed, excepting that the tendency to fusion was not so marked in this case as with the sodium salts. The volatilized arsenic acid gave 0.1094 gram of magnesium pyro-salt, thus falling short of the theoretical amount by 0.0006 gram. The residual magnesium pyrophosphate weighed 0.1105 gram. This approaches the theoretical (0.1100 gram) so closely that the separation must be viewed as complete.

*Experiment 2.*—The same quantities of the two salts were taken in this trial. Instead of 0.1100 gram of pyrophosphate actually taken the found salt equaled 0.1108 gram. The difference between the arsenic salt used and the quantity of it, which was carried out of the mixture by the gas, equaled 0.0009 gram. An examination of the non-volatilized phosphate showed it to be free from arsenic. Lead arsenate was very readily transposed by the acid into lead chloride, and the volatile arsenic derivative.

Lead arsenate.	Obtained.	Lead chloride. Required.
<i>Experiment 1.</i> —0.2965 gram	gave 0.2746 gram	0.2747 gram.
" 2.—0.3608 "	" 0.3347 "	0.3343 "

The residual lead chloride was dissolved in water, and the aqueous solution introduced into a Marsh apparatus. Not a trace of arsenic was found in this way. Upon adding a very slight amount of lead arsenate to the solution the mirror and spots of arsenic were almost immediately observed. The complete transposition of this salt induced us to execute a third trial in which we not only weighed the residual lead chloride and

found it satisfactory, but also determined the arsenic which had been volatilized.

Lead arsenate.	Magnesium pyroarsenate.	
	Found.	Calculated.
0.2965 gram gave.....	0.1022 gram.	0.1028 gram.

Two portions of a mineral containing lead, arsenic acid, and phosphoric acid, were exposed to the action of the acid gas. The volatilized arsenic equaled in (a) 10.42 per cent, and in (b) 10.39 per cent. None remained in the residue contained in the boat.

Experiments have not yet been made with antimonates.

Separations of vanadic and arsenic acids from tungstic and chromic acids are now being carried out, and with encouraging results. The action of hydrobromic, hydriodic and hydrofluoric acid in gas form upon vanadates, nitrates, arsenates and phosphates, has received attention with results which will appear later.

UNIVERSITY OF PENNSYLVANIA.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 5.]

### URANIUM OXYNITRIDE AND URANIUM DIOXIDE.

BY EDGAR F. SMITH AND J. MERRITT MATTHEWS.

Received May 31, 1895.

THE action of ammonia upon molybdenyl ( $\text{MoO}_2\text{Cl}_2$ ) and tungstyl ( $\text{WO}_2\text{Cl}_2$ ) chlorides has received attention in this laboratory. To complete the study of Group VI in this direction, uranyl chloride ( $\text{UO}_2\text{Cl}_2$ ) was prepared, placed in a porcelain boat and heated in a glass tube in a current of dry ammonia. At a comparatively moderate temperature the material began to take on a dark color, and copious fumes of ammonium chloride were evolved. The heat was raised and continued until the ammoniacal salt was no longer produced. The residue was dull black in color. When fused in a nickel crucible with caustic potash, ammonia was slowly evolved. A portion of the substance introduced into aqueous silver nitrate caused the separation of a beautiful deposit of brilliant crystals of metallic silver. Chlorine was not found in the compound. When it was heated with sulphuric acid (1:2) in a sealed tube, complete solution ensued. Upon titration with standardized potassium permanganate, the presence of 6.83 per cent. of dioxide was disclosed. No hydro-

gen was discovered in the material examined for it. Four analyses were made and resulted as follows:

0.2311	gram of material gave	84.81	per cent.	uranium.
0.3139	" " " "	2.19	" "	nitrogen.
0.2412	" " " "	84.87	" "	uranium.
0.1868	" " " "	2.24	" "	nitrogen.

The mean of the uranium and nitrogen determinations was 84.84 per cent. uranium and 2.21 per cent. nitrogen, leaving a difference of 12.95 per cent. for oxygen. The formula we have deduced from these figures is  $U_{11}N_2O_{11}$ , which requires 84.88 per cent. uranium, 2.25 per cent. nitrogen, and 12.87 per cent. oxygen.

Uhrlaub<sup>1</sup> mentions an oxynitride of uranium which from its analysis approximates the formula  $U_5N_2O_{11}$ .

From further experiments made by us it is evident that these oxynitrides are bodies of extremely variable constitution, dependent upon the temperature and length of time to which the uranium body is exposed to the action of the ammonia. This conduct was also observed to prevail with the corresponding derivatives of both molybdenum and tungsten.

*Preparation of Uranium Dioxide.*—The preparation of this compound has been the subject of much discussion. It will be remembered that this is the oxide long looked upon as metallic uranium. Zimmermann<sup>2</sup> found that it resulted upon merely heating the oxide  $U_3O_8$  in indifferent gases, such as carbon dioxide. Others have recommended the ignition of urano-uranic oxide in hydrogen, or together with sulphur, or with sulphur and ammonium chloride. We submit the course by which we obtained it. The oxide  $U_3O_8$  was intimately mixed with a large excess of dry ammonium chloride in a porcelain crucible, and this then placed in a larger Hessian crucible and surrounded with closely packed charcoal. The crucibles were heated in a wind furnace at almost a white heat for about six hours. A reddish brown substance remained. It contained no nitrogen or chlorine. Two portions of it were dissolved in nitric acid and the uranium determined with these results: 88.23 per cent. and

<sup>1</sup> Verbindungen einiger Metalle mit Stickstoff, Göttingen, 1859.

<sup>2</sup> Annalen, 232, 283.

88.00 per cent., giving as a mean 88.12 per cent. A third portion, weighing 0.3363 gram, was heated for fifteen minutes over a Bunsen flame; the increase in weight was 0.0119 gram, and heating again for forty-five minutes there resulted an alteration of only 0.0011 gram, after which the weight continued constant. The total increase of the material taken by its conversion into urano-uranic oxide, was therefore 0.0130 gram, while the calculated increase should be 0.0132 gram.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 6.]

### THE SEPARATION OF IRON FROM BERYLLIUM.

By ELIZABETH A. ATKINSON AND EDGAR F. SMITH.

Received May 31, 1895.

THIS separation is generally effected through the solubility of beryllium hydroxide in ammonium carbonate. It is, however, not always satisfactory, and any method affording better results will be of interest to the analyst.

Ilinski and v. Knorre<sup>1</sup> called attention to the use of nitroso- $\beta$ -naphthol in analytical work. For example, they separated cobalt from nickel and iron from aluminum by means of this reagent. Inasmuch as their study has not been continued, it seemed to us of interest to ascertain whether or not the same reagent could be used for the separation indicated at the head of this communication. We used the following solutions: (1) a fifty per cent. acetic acid solution of the nitroso- $\beta$ -naphthol, (2) a ferric solution of which ten cubic centimeters contained 0.1278 gram of ferric oxide, and finally a beryllium chloride solution of which ten cubic centimeters contained 0.1248 gram.

The first step taken was to learn how completely the iron was precipitated by the proposed reagent. To this end ten cubic centimeters of the ferric solution ( $=0.1278$  gram  $\text{Fe}_2\text{O}_3$ ) were diluted with two hundred cubic centimeters of distilled water, and one hundred and twenty-five cubic centimeters of the nitroso- $\beta$ -naphthol added to the cold liquid, which was then allowed to stand for a period of twenty-four hours. The iron precipitate was then filtered out, washed at first with fifty per cent. acetic acid, and subsequently with water, until a few drops of the washings left no residue upon evaporation and ignition upon a strip

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 699, 2728.

of platinum. After the iron nitroso- $\beta$ -naphthol had dried it was mixed with an equal amount of pure oxalic acid, and the filter folded up over the mixture, which was then carefully heated in a weighed porcelain crucible. The heat at first was moderate, but gradually increased until all the carbon had been burned off. These are practically the precautions which were recommended by Ilinski and v. Knorre, so that our experience corroborates that given by these chemists.

The results obtained by us are:

1. 0.1277 gram of ferric oxide.
2. 0.1283   "   "   "   "
3. 0.1277   "   "   "   "

The theoretical ferric oxide equaled 0.1278 grams.

Upon treating ten cc. of the beryllium solution just as described under the iron, no evidence of precipitation was observed even after the expiration of forty-eight hours.

The real object of our study was the separation of the iron from the beryllium. In following out this idea we proceeded in the following manner: Ten cc. of the ferric salt (=0.1278 gram of ferric oxide) and an equal volume of the beryllium solution, equal to 0.1248 gram beryllium oxide, were diluted to two hundred cc. with distilled water. The nitroso- $\beta$ -naphthol solution was added to this cold mixture. After standing twelve hours the ferric compound was filtered out and disposed of as above described. The ferric oxide found was:

1. 0.1277 gram,
2. 0.1275   "
3. 0.1277   "

instead of the theoretical 0.1278 gram.

Efforts made to precipitate uranium salts with this reagent resulted negatively. The substitution of an alcoholic for an acetic acid solution of the reagent made no difference.

We also found that nitroso- $\beta$ -naphthol does not precipitate solutions of cerous salts, of lanthanum ammonium nitrate, of praseodymium nitrate, of neodymium nitrate, of terbium, of erbium, or of sodium molybdate or tungstate. Zirconium chloride gave an orange-colored precipitate, and ceric ammonium nitrate a bright scarlet, flocculent precipitate, which was, however, far from being complete.

## ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINEBARGER.

[Continued from page 652]

TABLE VII.

*Vapor-Tensions of Mixtures of Toluene and Chloroform at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.*

Molecules CHCl <sub>3</sub> in 100 mole- cules of liquid mixture.	Molecules CHCl <sub>3</sub> in 100 mole- cules of gaseous mixture.	Grams CHCl <sub>3</sub> in vapor.	Grams C <sub>7</sub> H <sub>8</sub> in vapor.	Ten- sion of CHCl <sub>3</sub> in mm.	Ten- sion of C <sub>7</sub> H <sub>8</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
28.74	65.29	0.4856	0.1994	64.7	34.4	1040	747	24
60.43	89.20	1.3578	0.1270	160.9	19.5	1031	754	23

TABLE VIII.

*Vapor-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*

Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>6</sub> H <sub>6</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>6</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
7.21	9.66	0.1741	0.8260	14.5	135.4	1205	762	18
18.68	20.54	0.3931	0.7561	32.5	125.5	1205	758	20
28.00	35.71	0.6267	0.5730	60.0	105.0	1016	756	12
50.19	55.03	1.1231	0.4666	91.3	75.6	1201	762	19
63.88	65.27	1.2699	0.3431	103.1	54.5	1219	760	27
77.89	83.01	1.5321	0.1669	117.6	31.8	1034	754	26

TABLE IX.

*Vapor-Tensions of Mixtures of Toluene and Carbon Tetrachloride at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*



Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>7</sub> H <sub>8</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>7</sub> H <sub>8</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
30.69	58.19	0.4754	1.2046	51.5	37.0	1016	756	12
53.85	67.86	0.9305	0.1260	78.3	22.3	1022	758	17
60.00	83.67	0.9624	0.1126	99.1	19.4	1020	759	14
91.87	97.22	1.6063	0.0281	155.1	4.5	1017	756	13

TABLE X.

*Vapor-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34.8°.*

*Vapor-Tension of Nitrobenzene at 34.8° is 1.16 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*

Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
5.37	93.51	0.3095	0.0175	18.9	1.3	1973	760	20
50.73	94.47	1.1111	0.0489	113.9	6.2	1020	756	12
73.54	96.09	1.4420	0.0471	141.5	5.6	1022	753	18
95.21	98.61	1.7798	0.0190	167.6	2.3	1022	753	18

#### 10. INFLUENCE OF TEMPERATURE ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

It is a well-known fact that the higher the temperature the greater the vapor-tension; this is true of mixtures of liquids as well as of the liquids themselves. It may be, now, that the vapor-tensions of mixtures of volatile liquids exhibit a deportment varying with the temperature; but if it can be shown that change of temperature is without influence upon the nature of the phenomenon presented by the vapor-tensions of such mixtures, the experimental investigation of the subject is much simplified, for theoretic conclusions based on data found at a certain temperature can be at once applied to other temperatures, so that the investigation of the vapor-tensions of mixtures of various concentrations at one temperature suffices for the discussion and elucidation of the entire problem. Material which furnishes an answer to the question as to whether temperature has an influence upon the vapor-tensions of mix-

tures of volatile liquids can be found in the papers of Regnault (*loc. cit.*), Raoult (*loc. cit.*), and Brown (*loc. cit.*).

Regnault's determinations were made through a considerable range of temperature, and, although, at most only three different concentrations were examined, it is possible by rearranging them to get an answer to our query. The mixtures which can be utilized are five in number,—two mixtures of carbon bisulphide and ethyl oxide, whose vapor-tensions were determined by the static method, and one mixture of the same liquids, the vapor-tension of which was determined by the dynamical method; and two mixtures of carbon bisulphide and carbon tetrachloride of which the vapor-tensions were investigated by the static method.

The first mixture of carbon bisulphide and ether was made up of sixty-two volumes of the first liquid and thirty-eight volumes of the second, ("Mélange de 62 sulphure de carbone et 38 d'éther, en volumes"), and eleven determinations of its vapor-tension were made in the temperature interval  $4.72^{\circ}$  to  $39.44^{\circ}$ . If we put the specific gravity of Regnault's carbon bisulphide at 1.27, and that of his ether at 0.78, the mixture contained by weight 27.35 per cent. of ether, and 72.65 per cent. of carbon bisulphide; or a hundred molecules of the mixture contained 27.20 molecules of ether and 72.80 molecules of carbon bisulphide. The second mixture was prepared by mixing fifty-six volumes of ether and forty-one volumes of carbon bisulphide ("Mélanges de 56 éther et de 41 sulphure de carbone en volumes"). Thirteen determinations were made of the vapor-tensions of this mixture at temperatures varying from  $8.01^{\circ}$  to  $38.18^{\circ}$ . One hundred parts by weight contained then 45.61 parts of ether and 54.39 parts of carbon bisulphide; and one hundred molecules of the mixture contains 46.29 molecules of ether and 53.71 molecules of carbon bisulphide.

The third mixture of carbon bisulphide and ether was made up of equal volumes of each; ("Mélange, a volume éguax, de sulphure de carbon et d'éther") about twenty-five measurements were made in the temperature interval from  $20.81^{\circ}$  to  $121.48^{\circ}$ . The percentage composition of the mixture is 61.95 per cent. of carbon bisulphide and 38.05 per cent. of ether, and the molecu-

lar percentage composition is 61.32 molecules of carbon bisulphide and 38.68 molecules of ether.

The first mixture of carbon tetrachloride and carbon bisulphide contained equal volumes of the two liquids; ("Mélange de volumes égaux de chlorure de carbone et de sulphure de carbone") ten determinations of its vapor-tension were made at temperatures varying from  $8.75^{\circ}$  to  $48.43^{\circ}$ . If we put the specific gravity of Regnault's carbon tetrachloride as equal to 1.62, and that of his carbon bisulphide as equal to 1.27, the percentage composition by weight of the mixture is 56.06 per cent. of carbon tetrachloride and 43.94 per cent. of carbon bisulphide; and one hundred molecules of the mixture contain 61.2 molecules of the first-named liquid and 38.8 molecules of the last-named.

In indicating the composition of the second mixtures Regnault uses the following words: "Mélange de 60 parties sulphure de carbone et de 145 chlorure de carbone." There is doubt here as to whether Regnault means by "parties," parts by weight or by volume. This is the only place where this form of expression is used, and in the other cases, it is expressly stated that the units of measure are volumes. I take it, then, that in this case parts by weight are to be understood, and in the sequel it will be seen that the regularity of the data as represented graphically renders this understanding of the matter warranted. At any rate, the difference between the results of calculations with volumes or weights as bases is not very great, so that there is not much danger of committing any very gross error. By weight the percentage composition of this mixture is 70.73 per cent. of carbon tetrachloride and 29.27 per cent. of carbon bisulphide, while one hundred molecules of it contain 65.47 molecules of carbon tetrachloride and 34.53 molecules of carbon bisulphide. I give also the percentage molecular composition on the assumption that Regnault's "parties" means parts by volume; one hundred molecules of the mixture contain 54.47 molecules of carbon tetrachloride and 45.53 molecules of carbon bisulphide.

In order to transform Regnault's data, the following procedure was gone through with: In a system of coordinates with temperatures as abscissas and vapor-tensions as ordinates, his measurements were plotted on a large scale; as might be expected

of any of Regnault's experimental work, the points fell very close to a regular curve. At points at this curve corresponding to  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ , etc., the value of the ordinates was carefully taken, that is, the vapor-tensions for each of the above temperatures. In this way data were obtained by means of which isothermal curves were drawn in a system of coordinates with concentrations as abscissas and vapor-tensions as ordinates.

An inspection of the isothermal curves shows that no appreciable influence of temperature manifests itself; the vapor-tension of the more volatile component of the mixture increases, indeed, more rapidly than that of the less volatile, but this does not affect the contour of the curve, its inclination alone being somewhat altered.

Raoult<sup>1</sup> made a special study of the possible influence of temperature upon the vapor-tensions of mixtures of ether with each of the following liquids almost nonvolatile at low temperatures: turpentine, aniline, perchlorethane, and benzoic acid, the temperature interval being from  $0^{\circ}$  to  $22^{\circ}$ . The results of his experiments permitted him to draw the definite conclusion that in the above temperature interval the vapor-tension is quite independent of the temperature.

The experiments of Brown<sup>2</sup> on the boiling-points of carbon bisulphide and carbon tetrachloride may be brought forward as evidence that the influence of the temperature on the vapor-tensions of mixtures of normal liquids is very slight; he found the curves, sketched with percentage composition on the axis of abscissas, and boiling-points on the axis of ordinates, for the pressures 747 to 760, and 430 to 432 mm. to be practically parallel.

From the above considerations, we may conclude that temperature has but a vanishing influence upon the vapor-tensions of mixtures of normal liquids; that is to say, although the higher the temperature, the greater the vapor-tension, the regularities found and the laws deduced from observations made at any one temperature are, without question, applicable to any other temperature, which, however, be it remarked as a caution, should probably not be too different from that of the observations.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

XI. RELATIONS BETWEEN THE VAPOR-TENSIONS, PARTIAL  
AND TOTAL, AND THE CONCENTRATION OF THE  
LIQUID PHASES.

We remark first, that the tension of the mixed vapor emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure of either component, of any mixture, is always less than the vapor-tension of the component in a state of purity;<sup>1</sup> these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very similar in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realized, for the vapor-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissas = molecular percentages; ordinates = vapor-tensions) of the determinations, these fall upon, or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapor-tensions of each of the pure liquids. In order to find the vapor-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapor-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissas cuts this line, the value of the ordinate corresponding to the point of intersection gives

<sup>1</sup> This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

the vapor-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalizations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behavior approaches most nearly that theoretically predicted.

In the second of our classes we find a different behavior. When chloroform is added to benzene or to toluene, the total vapor tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from fifty to sixty molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapor-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed eighty. The depression of the vapor-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than twenty molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures, we meet with a different behavior. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapor-tensions of the mixed liquids until towards the abscissas value of eighty; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapor-tension of the pure hydrocarbon, benzene, or

toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behavior is general, and that in all binary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behavior as regards partial vapor-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapor-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behavior of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride,

does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult<sup>1</sup> has made an elaborate study of the total vapor-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The curves are, if we regard the right-hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapor-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissas value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behavior was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly, I have recalculated his data so as to get them into a form comparable with mine. These recalculated data are given in the following small tables:

TABLE A.

*Vapor-Tensions of Solutions of Turpentine in Ether at 16.2°.*

*Vapor-Tension of Turpentine at 16.2° is four mm. of Mercury.*

*Vapor-Tension of Ether at 16.2° is 377 mm. of Mercury.*

Molecules of turpentine in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of turpentine in 100 molecules of solutions.	Vapor-tension in mm. of mercury.
5.9	354	35.5	255
12.1	332	47.9	212
23.4	294	64.5	159

TABLE B.

*Vapor-Tension of Solutions of Nitrobenzene in Ether at 16.0°.*

*Vapor-Tension of Nitrobenzene at 16.0° is four mm. of Mercury.*

*Vapor-Tension of Ether at 16.0° is 374 mm. of Mercury.*

Molecules of nitrobenzene in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of nitrobenzene in 100 molecules in solution.	Vapor-tension in mm. of mercury.
6.0	353	56.2	232
17.9	321	75.9	166
35.5	278	84.0	132

<sup>1</sup> *Loc. cit.*



TABLE C.

*Vapor-Tensions of Solutions of Aniline in Ether at 15.3°.**Vapor-Tension of Aniline at 15.3° is four mm. of Mercury.**Vapor-Tension of Ether at 15.3° is 364 mm. of Mercury.*

Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.
3.8	349	20.5	292
7.7	335	49.6	210
14.8	308	68.7	147

TABLE D.

*Vapor-Tension of Solutions of Methyl Salicylate in Ether at 14.2°.**Vapor-Tension of Methyl Salicylate at 14.2° is four mm. of Mercury.**Vapor-Tension of Ether at 14.2° is 306 mm. of Mercury.*

Molecules of methyl salicylate in 100 mole- cules of solution.	Vapor-tension in mm. of mercury.	Molecules of methyl salicylate in 100 mole- cules of solution.	Vapor-tension in mm. of mercury.
1.1	344.6	23.2	281
2.1	343.6	49.0	208
4.8	332.0	77.0	125
9.2	316.0	85.0	101
15.1	301.0	....	....

TABLE E.

*Vapor-Tensions of Solutions of Ethyl Benzoate in Ether at 11.7°.**Vapor-Tension of Ethyl Benzoate at 11.7° is three mm. of Mercury.**Vapor-Tension of Ether at 11.7° is 313 mm. of Mercury.*

Molecules of ethyl ben- zoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of ethyl ben- zoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
4.9	296	53.0	167
9.6	286	75.5	94
27.1	235	94.4	39

If these results be plotted in a system of coordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

## XII. RELATIONS BETWEEN THE CONCENTRATIONS IN THE GASEOUS AND LIQUID PHASES.

The relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of coordinates, of which the axis of abscissas is taken for the rep-

resentation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. In Fig. V are drawn these curves, the data being taken from the first two columns of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above, when it is more volatile.

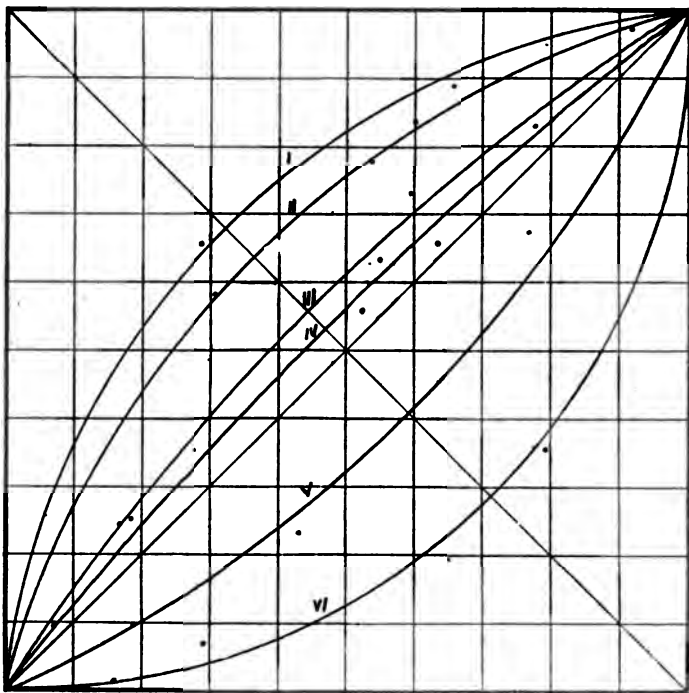


FIG. 5.—RELATIONS BETWEEN THE CONCENTRATIONS IN LIQUID AND GASEOUS PHASES.

Abscissas = molecules of one liquid in 100 molecules of mixture of liquids.

Ordinates = molecules of one vapor in 100 molecules of mixture of vapors.

Curve I.....	Toluene-chloroform.
"    II.....	Toluene-carbon tetrachloride.
"    III.....	Benzene-chloroform.
"    IV.....	Benzene-carbon tetrachloride.
"    V.....	Toluene-monochlorobenzene.
"    VI.....	Benzene-monochlorobenzene.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal liquids with the same vapor tension would give off vapors with identical composition in both liquid and gaseous state.

#### XIV. HEAT OF DILUTION AND SOLUTION. IDEAL CONCENTRATED SOLUTIONS.

Kirchoff<sup>1</sup> developed by thermodynamic considerations an equation showing a relation between the heat of dilution of a solution and its vapor-tension. If we designate by  $dQ$ , the heat brought into play when the small quantity  $dm$  of water is added to the solution, and if  $p'$  represent the vapor-tension of the solution and  $p$  that of the pure solvent, while  $T$  is the temperature and  $R$  the gas constant measured in units of heat, he found that

$$(A) \quad \frac{dQ}{dm} = RT^2 \frac{d \log \frac{p'}{p}}{dT}$$

This equation was more particularly developed for the case of solutions of fixed substances, and has in fact been compared with the experiments done on the vapor-tensions and heat of dilution of sulphuric acid dissolved in water. Recently, however, three quite similar formulas have been obtained which apply directly to the heat given out or taken in when two liquids are mixed, and the corresponding changes of the elastic forces of the vapors. LeChatelier<sup>2</sup> developed for the case of a mixture of two liquids the formula

$$(B) \quad n \frac{dp}{p} + n' \frac{dp'}{p'} - 500 \frac{n L_1 + n' L_2 + \lambda}{T^2} dT = 0$$

wherein  $p$  and  $p'$  are vapor-tensions,  $L_1$  and  $L_2$ , latent heats of vaporization,  $\lambda$  the heat disengaged on mixing  $n + n'$  molecules of two liquids, and  $T$  is the temperature. As is readily seen, this formula is a special adaptation of Kirchoff's formula; in reality, they may be considered as expressing similar relations.

Nernst<sup>3</sup> by carrying out a closed cycle in the thermodynamic

<sup>1</sup> Ueber einen Satz der Mechanischen Wärmetheorie und einige Anwendungen desselben: *Ann. der Phys. Pogg.*, 103, 177, 1885.

<sup>2</sup> *Loc. cit.*, 281.

<sup>3</sup> *Theor. Chem.*, 102-105.

sense of the term, in which semi-permeable membranes play a conspicuous rôle, has arrived at this equation :

$$(C) \quad Q_{(x)} = -RT^2 \frac{d}{dT} \left( \ln \frac{p_0}{p} + x \ln \frac{P_0}{P} \right)$$

in which  $Q_{(x)}$  is the heat of mixture,—equal to the decrease of the internal energy,— $R$  and  $T$  have the same signification as in formula (A),  $p_0$  and  $P_0$  are the vapor-tensions of the pure liquids, and  $p$  and  $P$  the vapor-tensions at the moment of mixing, and  $x$  the number of molecules of one component to one molecule of the other. As is evident, this formula is quite similar to that of Kirchoff, which, Nernst claims, is but a special case of his more general one.

Duhem<sup>1</sup> has, by the application of the thermodynamic potential, which has proven so fruitful in his hands, developed the following formulas, each of which is applicable to the heat evolved or absorbed when to a solution of two liquids, certain masses of either liquid,  $\delta M_1$  or  $\delta M_2$ , are added :

$$(D) \quad EL_1 = \frac{4 \Sigma R}{\alpha_1 \omega_1} T^2 \frac{d}{dT} \log \frac{p_1(x, T)}{P_1(T)},$$

$$(D \text{ bis}) \quad EL_2 = \frac{4 \Sigma R}{\alpha_2 \omega_2} T^2 \frac{d}{dT} \log \frac{p_2(x, T)}{P_2(T)};$$

in the formulas  $E$  is the mechanical equivalent of heat ;  $L_1$  and  $L_2$ , heats of solution ;  $\Sigma$  the specific volume of hydrogen in normal conditions of temperature and pressure ;  $R$  a constant having the same value for all ideal gases ;  $\alpha_1$  and  $\alpha_2$ , atomicities ;  $\omega_1$  and  $\omega_2$ , molecular masses,  $T$  the temperature ;  $p_1$  and  $p_2$ , the vapor-tensions of the solutions ; and  $P_1$  and  $P_2$ , the vapor-tensions of pure liquids. It is at once apparent that this equation, if Duhem's complete, but rather prolix manner of writing be suitably transformed, is identical with the one developed by Kirchoff.

An important conclusion can be drawn from the above equations, in case the heat of solution turns out to be equal to zero ; then,  $\frac{d}{dT} \log \frac{p'}{p}$  becomes equal to zero too, and the ratio  $\frac{p'}{p}$  is independent of the temperature. That, in reality, to a very close

<sup>1</sup> Dissolutions et Mélanges ; Troisième Mémoire ; Les Mélanges Doubles : Travaux et Mémoires des Facultés de Lille, 100, 1894.

approximation such is the condition of affairs for certain dilute solutions has been known since 1857; and such solutions are said to follow the law of von Babo,<sup>1</sup> which says that the heat of dilution must be zero.

Now we have found that the mixtures of the first class at least, that is, those made up of benzene, toluene, monochlor- and monobrombenzene, have vapor-tensions which are practically independent of the temperature, that is, the fraction  $\frac{p'}{p}$  has the same value for all temperatures. It follows then that no thermal change should accompany the act of mixing of the liquids; their heat of solution or dilution is zero. No experiments so far as I know, which can give evidence as to the correctness of this statement, have been performed; but there can be no questioning of the truth of the relation developed and it is not at all probable that the determinations of the vapor-tensions are much in error.

In order to put this prevision of theory to the test of experience, I have made a number of determinations of the thermal effect of mixing liquids, especially those of the first class. Two methods were employed, that requiring the use of a Bunsen's ice-calorimeter, and that depending upon the measurement of the change of temperature.

The ice-calorimeter which was employed was of comparatively large size, the inner tube having an internal bore of twenty mm., and a length of 200 mm. within the outer tube. The calorimeter was filled, set up, and manipulated nearly as recommended by Schuler and Wartha, the amount of mercury absorbed or expelled being weighed.

After the calorimeter had been gotten into normal working condition, it was found that a continuous formation of ice was occurring around the inner tube. The amount was, however, not only slight, but also very constant, so that it was possible to apply an entirely reliable correction for it.

The cooling of the liquids to 0° and their subsequent mixing was accomplished in the following manner: A thin glass tube closed at one end and of such internal diameter as to permit of

<sup>1</sup> Berichte über die Verhandlungen der Gesellschaft für Beförderung der Naturwissenschaften zu Freiburg in Brisgau. January, 1857, 282.

its being easily but snugly slipped into the inner tube of the calorimeter was of such length that about an inch of it projected out of the calorimeter. A cylindrical pipette, fitting easily into the glass tube just described, had its lower orifice directly below the bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the orifice; a bit of rubber tubing was slipped over the glass rod, which could be pushed down between the rod and the stem of the pipette, thus closing the latter above. The pipette was held in place in the tube by means of a tightly fitting cork.

A piece of aluminum foil was for about two-thirds of its length cut into in several places along each side nearly to the middle, and the parts thus formed were so bent that, when the other third of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held by its own elasticity, they formed a number of small paddles, those on one side directed upwards, those on the other directed downwards. Such a stirrer permits of a rapid and complete mixing of liquids.

To make a determination, a certain amount of one liquid is introduced into the pipette and weighed therein. The other liquid is weighed in the tube which is provided provisionally with a cork. The aluminum stirring contrivance is then slipped over the bulb of the pipette, and the latter passed into the tube, being held in place by a tightly fitting cork; the pipette is not pushed deep enough into the tube to have its orifice dip in the mixture of liquids, and the paddles reach to the bottom of the tube. A weighed dish of mercury is allowed to catch the expelled mercury of the empty calorimeter for exactly half an hour before the liquids are introduced; by this means the calorimeter correction just before the determination is obtained. After the introduction of the tube and pipette, the calorimeter is allowed for a half hour or so to get again into its normal state. After this has come to pass, a fresh dish of mercury is put under the mercury tube, the cork holding the pipette is lifted, the glass rod is raised a little, and the liquid in the pipette allowed to run out. The pipette is then tightly closed, and twisted around for a half minute or so to thoroughly mix the two liquids. The cork is

again inserted in the tube, and the whole left for exactly half an hour. At the expiration of that time, the mercury vessels are changed, and the calorimeter left to itself for another half hour, when the mercury vessels are again changed, and the tube and pipette removed. The pipette is again weighed, and the difference between the two weights gives the amount of liquid. The amount of mercury expelled from the apparatus during the last half hour should, if the thermal equilibrium, disturbed by the heat evolved or absorbed by the mixture of the liquids, has reestablished itself, and if no change in the velocity of the freezing of the water itself has supervened, be equal to the amount expelled in the first half hour; in other words, the corrections in each case should be equal. This I found to be invariably the case. The heat effect of the mixing of the liquids is accordingly to be obtained from the excess or deficit of the amount of mercury expelled or absorbed in the next to the last half hour compared with that expelled during the first and the last half hours. This difference divided by 0.01544 gives the number of lesser calories measuring the heat effect of the mixing of the liquids.

By a most scrupulous attention to details in manipulation and to observance of time, as well as to care in weighing, I think that the determinations are exact to one-tenth calorie, and even to less than that.

I give in the following experiments the data obtained in the determination of the thermal effect of mixing such liquids as have been found in the foregoing pages to show the simplest behavior, and have hence been grouped into the first class. The negative sign before a datum is indicative of an absorption of heat, and consequent formation of ice and expulsion of mercury, while the positive sign indicates an evolution of heat, etc.

*Experiment 1.*—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene .....	3.0028 grams.
Toluene .....	4.3032 "
Calorimeter correction in weight of mercury.....	—0.0013 "
Weight of mercury moved .....	—0.0018 "
" " " " due to mixing of liquids .....	—0.0005 "
Thermal effect measured in lesser calories.....	—0.032 "

*Experiment 2.*—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene .....	3.7715 grams.
Toluene .....	4.2190 "
Calorimeter correction in weight of mercury .....	—0.0014 "
Weight of mercury moved .....	—0.0020 "
" " " " due to mixing of liquids .....	—0.0006 "
Thermal effect measured in lesser calories .....	—0.033 "

*Experiment 3.*—Heat effect of mixing brombenzene and toluene:

Brombenzene .....	4.9530 grams.
Toluene .....	4.3680 "
Calorimeter correction in weight of mercury .....	—0.0009 "
Weight of mercury moved .....	—0.0020 "
" " " " due to mixing of liquids .....	—0.0011 "
Thermal effect measured in lesser calories .....	—0.072 "

*Experiment 4.*—Heat effect of mixing brombenzene and toluene:

Brombenzene .....	1.1611 grams.
Toluene .....	7.3887 "
Calorimeter correction in weight of mercury .....	—0.0010 "
Weight of mercury moved .....	—0.0005 "
" " " " due to mixing of liquids .....	+0.0005 "
Thermal effect measured in lesser calories .....	+0.032 "

Inasmuch as benzene solidifies at a temperature somewhat above that of melting ice, was not possible to carry out determinations in the ice-calorimeter with it in the pure state; accordingly I prepared a mixture containing 97.37 per cent. benzene and 2.63 per cent. chlorbenzene, which was used in experiment five.

*Experiment 5.*—Heat effect of mixing benzene and chlorbenzene:

Mixture of benzene and chlorbenzene .....	3.0208 grams.
Chlorbenzene .....	6.3470 "
Calorimeter correction in weight of mercury .....	—0.0013 "
Weight of mercury moved .....	—0.0030 "
" " " " due to mixing of liquids .....	—0.0017 "
Thermal effect measured in lesser calories .....	—0.101 "

An inspection of the above data shows that none of the heat effects is much above the limit of accuracy of which the method was judged capable. It was deemed worth while, however, to make some determinations of the heat effects brought about by



mixing liquids by means of thermometric measurements, especially for mixtures of benzene and other liquids, as benzene in the pure state could not be used in the ice-calorimeter. The apparatus used, although simple, is capable of telling with considerable accuracy whether there occurs a change in temperature when two liquids are mixed. It consisted of a large U tube, in one branch of which was fitted a thermometer graduated in hundredths of a degree, such as described by Beckmann,<sup>1</sup> and recommended for cryoscopic and ebullioscopic work, and in the other a pipette similar to the one described above in connection with the ice-calorimeter. The U tube had a very narrow side tube towards the top of one branch, which when stopped with cotton wool permitted the egress of air without any evaporation of the liquids in the large tube to speak of. The stirrer employed was similar to the one used with the pipette in the ice-calorimeter.

A weighed quantity of one liquid was put into the U tube, and a quantity of the other liquid was weighed in the pipette. The thermometer and pipette were put in the tube tightly by means of good corks, the whole apparatus supported on a retort stand, and wrapped snugly with a thick layer of cotton wool. The apparatus was then set in a room the temperature of which could be easily kept within twenty-five to thirty degrees C. for several hours. By working at this rather high temperature, the disturbing effect due to the proximity of the person of the operator was considerably lessened. When the apparatus had remained in the room for a couple of hours, the thermometer was read off at intervals of a minute for ten minutes, the contents of the pipette made to flow into the U tube, the two liquids were mixed as rapidly as possible by a twirling and up and down motion of the pipette, around which was clasped the aluminum stirrer, and then the temperature was read off at each minute for ten minutes longer. The pipette was then again weighed so as to get the actual amount of the liquid discharged by it, since it never occurred that it emptied itself completely.

The experiments carried out by means of this thermochemical apparatus limit themselves to mixtures of benzene with monochlorobenzene and with chloroform. They, together with those

<sup>1</sup> *Ztschr. phys. Chem.*, 2, 644, 1888.

carried out with the ice-calorimeter, are perhaps sufficient to serve as experimental corroboration of the theoretical relations between heat of solution and vapor-tension.

It is perhaps best to append the whole series of determinations in order that the reader may judge for himself of the accuracy of the results.

CHANGE OF TEMPERATURE ON MIXING FOUR GRAMS MONOCHLORBENZENE AND 26.524 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.242°	11	2.339°
2	2.258°	12	2.348°
3	2.272°	13	2.369°
4	2.291°	14	2.381°
5	2.307°	15	2.388°
6	2.318°	16	2.390°
7	2.330°	17	2.396°
8	2.344°	18	2.394°
9	2.352°	19	2.388°
10	2.365°	20	2.380°

CHANGE OF TEMPERATURE ON MIXING 6.55 GRAMS MONOCHLORBENZENE AND 17.54 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.591°	11	2.709°
2	2.603°	12	2.751°
3	2.618°	13	2.803°
4	2.622°	14	2.820°
5	2.630°	15	2.829°
6	2.638°	16	2.838°
7	2.641°	17	2.847°
8	2.649°	18	2.853°
9	2.651°	19	2.861°
10	2.655°	20	2.872°

CHANGE OF TEMPERATURE ON MIXING 10.86 GRAMS MONOCHLORBENZENE AND 7.31 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.830°	11	1.421°
2	1.803°	12	1.400°
3	1.790°	13	1.395°
4	1.775°	14	1.372°
5	1.762°	15	1.370°
6	1.760°	16	1.420°
7	1.761°	17	1.435°
8	1.733°	18	1.450°
9	1.710°	19	1.445°
10	1.691°	20	1.438°

CHANGE OF TEMPERATURE ON MIXING 12.81 GRAMS CHLOROFORM AND  
11.87 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.489°	11	3.316°
2	1.520°	12	3.348°
3	1.531°	13	3.321°
4	1.540°	14	3.280°
5	1.561°	15	3.262°
6	1.573°	16	3.236°
7	1.582°	17	3.186°
8	1.608°	18	3.160°
9	1.621°	19	3.138°
10	1.632°	20	3.132°

It is apparent from these results that the change of temperature when benzene and monochlorbenzene are mixed does not exceed but a few hundredths of a degree, and even when the relative amounts of the liquids are about the same the change is in one case positive, in another negative, so that it is perhaps legitimate to judge that the change of temperature is largely due to the probability that the two liquids are at slightly different temperatures to begin with, and that in reality no or but an exceedingly slight heat effect occurs when these two liquids are mixed.

In the mixing of benzene and chloroform, however, there is a considerable rise of temperature, as indeed might be expected, since mixtures of chloroform and benzene do not in their vapor-tensions present the simplest phenomena. I have experimented with several other mixtures of liquids not belonging to the first class, especially with the ice-calorimetric method, and have found that they present certain abnormalities, some absorbing heat, and some evolving heat; these determinations, together with certain theoretical considerations, will form the substance of a subsequent paper.

Considering the above experiments as a whole, we may conclude that they are in entire corroboration of the formulas (A), (B), (C), and (D).

Nernst<sup>1</sup> found by the comparison of the theoretical conclusions with certain experimental data that the maximum of work, ob-

<sup>1</sup> Ueber die mit der Vermischung konzentrierter Lösungen verbundene Aenderung der freien Energie: Sonderabdruck aus Nr. 12 der Nachrichten von der Königl. Gesellschaft der Wissenschaften zu Göttingen. v. J., 1892.

tainable by mixing two concentrated solutions with the same solvent, is "often" equal to the concurrent thermal change.

He then proposes to call "a homogeneous mixture of two substances, of which the maximum of work which can be obtained by a change of its composition, is measured by the concomitant thermal phenomena," an "ideal concentrated solution."

The contrast between "ideal dilute solutions" and "ideal concentrated solutions" is best shown by a consideration of the equation which rules over all Nature's happenings; this, according to Helmholtz,<sup>1</sup> is

$$F - Q = T \frac{\delta F}{\delta T}$$

wherein  $F$  represents the decrease in the "free energy" (*freie Energie*);  $Q$  that of the "total energy" (*Gesamtenergie*), and  $T$  the initial and final temperature, assumed to be the same in the operation under consideration. The characteristic of the "ideal dilute solutions" is that  $Q = 0$  and that of the "ideal concentrated solutions" is that  $F = Q$ .

My object in mentioning these acute distinctions by Nernst is to call attention to the fact that there are certain combinations of substances (liquids) which, when mixed, develop no or very little heat, no matter what the relative proportions may be; that is, there exist "ideal dilute solutions" which may have any composition whatsoever, or, in other words, concentrated solutions may often follow the laws supposed to belong exclusively to dilute solutions. It is questionable, then, whether the notion of "ideal concentrated solutions" is necessary in science.

#### 15. VAPOR-TENSIONS OF MIXTURES OF ACETIC ACID WITH BENZENE AND WITH TOLUENE.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work, our mode of calculation of the vapor-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures. Now acetic acid even in the vaporous condition is

<sup>1</sup> Zur Thermodynamik chemischer Vorgänge. Sitzungs-Berichte der Berliner Akademie, 22, 1882.

made up in part of polymerized molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula  $C_6H_8O_2$ . What the actual molecular mass of the gaseous acid at  $35^\circ$  and  $20^\circ$  is, can be easily calculated by the aid of the vapor-density determinations of Bineau<sup>1</sup> which are the more applicable to the case in hand as his vapor-density measurements were made under the same conditions as my vapor-tension determinations; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations, is 104 for  $35^\circ$  and 110 for  $20^\circ$ . It may be worth while to remark that an error of five in the molecular mass will not entail an error of one millimeter in the vapor-tension: we may with all confidence then adopt the above molecular masses of acetic acid in state of vapor as quite accurate.

The necessary data of the experiments are given in tables XI to XIII, the superscription to each vertical column renders any explanation of them here superfluous.

TABLE XI.

*Vapor-Tensions of Mixtures of Benzene and Acetic Acid at  $35^\circ$ .*

*Vapor-Tension of Benzene at  $35^\circ$  is 146 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at  $35^\circ$  is 26.5 mm. of Mercury.*

Per cent. of $C_6H_8O_2$ in liquid mixture.	Per cent of $C_6H_8O_2$ in gaseous mixture.	Grams of $C_6H_8O_2$ in va- por.	Grams of $C_6H_8O_2$ in va- por.	Tension of $C_6H_8O_2$ in mm.	Tension of $C_6H_8O_2$ in mm.	Volume of air in mm.	Barom- eter in mm.	Inter- nal pressure in mm.
6.44	2.45	0.0461	1.3759	3.5	140.0	1955	758	14
15.17	4.74	0.0834	1.3580	6.4	129.2	1958	758	15
37.10	8.25	0.0700	1.5840	10.5	117.0	1020	767	16
43.99	11.02	0.0867	0.5243	13.2	106.5	1019	766	16
49.86	12.26	0.0931	0.4849	14.0	103.1	1020	766	17
53.24	13.33	0.0969	0.4731	14.9	97.6	1020	766	17
54.65	13.82	0.0990	0.4630	15.3	97.3	1020	766	17
56.60	14.62	0.1063	0.4677	16.4	96.0	1020	766	17
73.87	20.18	0.1156	0.4585	18.4	72.7	1019	766	16
80.00	26.91	0.1351	0.2751	22.3	59.3	1020	766	17

TABLE XII.

*Vapor-Tensions of Mixtures of Benzene and Acetic Acid at  $20^\circ$ .*

*Vapor-Tension of Benzene at  $20^\circ$  is 75.6 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at  $20^\circ$  is 11.7 mm. of Mercury.*

<sup>1</sup> Recherches sur les Relations des Densités des Vapeurs avec les Équivalents Chimiques: *Ann. chim. phys.*, 18, 226, 1846.

Per cent. of $C_6H_4O_2$ in liquid mixture.	Per cent. of $C_6H_4O_2$ in gase- ous mixture.	Grams $C_6H_4O_2$ in va- por.	Grams $C_6H_4$ in va- por.	Tension of $C_6H_4O_2$ in mm.	Tension of $C_6H_6$ in mm.	Volume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
53.24	11.99	0.0440	0.2291	6.6	48.7	1018	760	16
80.00	21.97	0.0576	0.2100	9.1	33.0	1018	760	16
97.28	64.66	0.0674	0.0276	11.4	6.2	1018	760	16

TABLE XIII.

*Vapor-Tensions of Mixtures of Toluene and Acetic Acid at 35°.*

*Vapor-Tension of Toluene at 35° is 47.2 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.*

Per cent. of $C_6H_4O_2$ in liquid mixture.	Per cent. of $C_6H_4O_2$ in gase- ous mixture.	Grams $C_6H_4O_2$ in va- por.	Grams $C_6H_6$ in va- por.	Tension of $C_6H_4O_2$ in mm.	Tension of $C_6H_6$ in mm.	Volume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
49.00	32.66	0.0911	0.1661	15.0	31.8	1020	760	18
60.88	37.91	0.1025	0.1485	17.4	28.5	1020	760	18
83.37	56.36	0.1252	0.0858	22.2	16.7	1020	760	18

From the above data curves were constructed on a large scale with percentages of composition as abscissas and vapor-tensions as ordinates (one inch on the axis of abscissas corresponded to five per cent.; one inch on axis of ordinates to ten mm. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the coordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapor-tension of pure acetic acid at the temperature in question, *viz.*: 26.5 for 35°, and 11.7 for 20°, the acetic acid vapor-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene; the specific influence of the diluting liquid seems to be extremely slight, if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi*.

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to ten, twenty, thirty, ..... ninety per cent. of acetic acid; the data thus obtained are given in Table XIV.

TABLE XIV.

*Partial Pressures of Benzene, Acetic Acid, and Toluene.*

Per cent. of $C_2H_4O_2$ in liquid mixture.	Partial pressure of $C_2H_6$ at 35° in mm.	Partial pressure of $C_2H_4O_2$ at 35° in mm.	Partial pressure of $C_2H_6$ at 35° in mm.	Partial pressure of $C_2H_6$ at 20° in mm.	Partial pressure of $C_2H_4O_2$ at 20° in mm.
10	138.4	2.8	44.5	71.4	1.2
20	130.9	5.6	41.6	67.5	2.3
30	122.2	8.2	38.6	63.1	3.5
40	112.6	11.1	35.0	58.2	4.8
50	102.4	13.6	31.9	53.2	6.0
60	90.7	16.2	27.8	47.1	7.2
70	76.7	19.1	23.1	40.1	8.4
80	59.1	21.7	18.4	31.1	9.6
90	35.1	24.2	11.1	18.5	10.7

#### 16. THE MOLECULAR MASS OF LIQUID ACETIC ACID AND A GENERAL METHOD OF DETERMINING MOLECULAR MASSES OF LIQUIDS.

The data given in the preceding section on the vapor-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalized so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:

In a system of coordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissas (twenty inches

long), and on the axis of ordinates, the vapor-tensions were taken from 0 to 150 mm. of mercury (fifteen inches long). A straight line was drawn from the point 100 on the axis of abscissas and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissas and 146 (benzene at  $35^\circ$ ), 75.6 (benzene at  $20^\circ$ ), and 47.2 (toluene at  $35^\circ$ ). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing ten, twenty, thirty, etc., per cent. of acetic acid, the data being taken from table XIV.

The value of the abscissas which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing  $m$  parts of a liquid  $A$ , having a molecular mass  $z$ , and  $n$  parts of a liquid  $B$ , having a molecular mass  $y$ ; the mixture is made up of  $r$  molecules of  $A$ , and  $s$  molecules of  $B$ . What is the value of  $x$  in the terms of  $y$ ,  $m$ ,  $n$ ,  $r$ , and  $s$ ?

In the case before us, we will take acetic acid for the liquid  $A$ , and benzene, or toluene as the case may be, for  $B$ ; then  $n$  is equal to  $(100-m)$ , and  $s$  to  $(100-r)$ .

It is easily found that the solution of our problem is

$$x = \frac{m s y}{r n} \text{ or } x = \frac{m (100-r) y}{(100-m)r}.$$

In the accompanying tables, XV, XVI, and XVII, the values of  $m$ ,  $r$ , and  $x$ , are given.

TABLE XV.

*Molecular Mass of Acetic Acid dissolved in Benzene at  $35^\circ$ .*

Percent $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	5.2	158
20	10.6	164
30	16.6	167
40	23.1	173
50	30.0	182
60	37.7	193
70	47.2	203
80	59.3	213
90	75.6	227
100	100.0	240



TABLE XVI.

*Molecular Mass of Acetic Acid dissolved in Benzene at 20°.*

10	5.1	161
20	10.5	166
30	16.2	172
40	22.6	177
50	29.6	186
60	37.2	198
70	46.7	208
80	58.7	218
90	75.2	231
100	100.0	244

TABLE XVII.

*Molecular Mass of Acetic Acid dissolved in Toluene at 35°.*

Per cent. of $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	6.1	159
20	12.4	163
30	19.0	168
40	26.5	170
50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering tables XV and XVII first, we see that the values of  $x$  are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for  $x$  fall out so nearly the same, for in the mixture of toluene and acetic acid, the differences of their vapor-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimeter in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determinations carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules

of acid is less, and hence their molecular mass is greater, than when the determinations were carried out at  $35^{\circ}$ . This is just what is to be expected for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of  $m$  and  $x$  given in the foregoing tables, in a system of coordinates with percentage composition as axis of abscissas and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at  $35^{\circ}$  practically coincides with that of the mixture of acetic acid and toluene at  $35^{\circ}$ , while the curve for the mixture of benzene and acetic acid at  $20^{\circ}$  is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at  $35^{\circ}$ , 240, and, at  $20^{\circ}$ , 244.

It is interesting to compare these results with those obtained by Ramsay and Shields.<sup>1</sup> These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits,  $16^{\circ}$  and  $46^{\circ}$ , was equal to 217.2 ( $60 \times 3.62$ ); although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised, which permits of the determination at any given temperature of the mass of the molecule.

<sup>1</sup> Ueber die Molekulargewichte der Flüssigkeiten. *Ztschr. phys. Chem.*, 12, 470, 1893.

It is founded on empirical results and depends upon no hypothesis other than the universally recognized one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analyzed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

#### RESUMÉ.

The main results of this article may be summed up as follows:

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.
2. Although the method can be said to give the vapor-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalizations.
3. A number of mixtures of representative liquids have been investigated as regards their vapor-tensions.
4. In some cases, extremely simple relations were found; in others, certain complexities presented themselves.
5. A recalculation of Regnault's determinations of the vapor-tensions of some mixtures of normal liquids as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solution showed that it was permissible to apply what was found true for any one temperature to any other.
6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the theoretical relations established by Planck and Nernst.
7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapor-tensions.
8. The vapor-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as

to permit of the determination of the molecular mass of the dissolved and liquid acid.

9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Dammour, *Ingénieur civil des Mines*, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. LeChatelier, *Ingénieur en chef des Mines*, whose wise direction and good counsel have been of great value to me throughout the work.

CHICAGO, May 1, 1895.

### WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

BY W. F. HILLEBRAND.

Received May 29, 1895.

DUNNINGTON<sup>1</sup> has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanite to meta-titanite acid, which does not afford a yellow color with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow color in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to

<sup>1</sup> This Journal, 13, 210.

an already peroxidized titanium solution weakens the color. For this reason it is necessary to take the greatest care to insure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the color even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, 5, 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralizing with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odor of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only two or three cc. of the peroxide are employed.

LABORATORY OF THE U. S. GEOLOGICAL  
SURVEY, WASHINGTON, D. C.

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[FROM THE CHEMICAL LABORATORY OF THE LANDWIRTSCHAFTLICHEN-  
LANDES-LEHRANSTALDT IN CZERNOWITZ.]

## THE VISCOSIMETRIC EXAMINATION OF BUTTER FOR FOREIGN FATS.

BY DR. NEWMANN WENDER.

Received July 1, 1895.

THROUGH a large number of investigations by Poisenille,<sup>1</sup> Girard, Hagenbach,<sup>2</sup> Graham, Rellstab, Pribram and Handl, Traube and Gartenmeister, to whose original investigations the reader is referred for the sake of brevity, it has been

<sup>1</sup> *Ann. der Phys. u. Chem. Pogg.*, 58, 424. *Ann. chim. phys.*, 64, 129.

<sup>2</sup> *Ibid.*, 99, 217.

established that a relation exists between the chemical composition of liquids and the velocity of transpiration just as there exists a relation between boiling-point and composition. There exists now a criterion for the purity of a substance, if a relation is found to exist between viscosity and boiling-point, at the same time, points of practical importance. From the investigations of Pribram and Handl it follows that observations of the specific viscosity or specific transmissibility of substances afford a hint as to the presence of adulterations and impurities, because these exert a decided influence upon the fluidity. The determination of the viscosity has found a practical value in the examination of oils and beer. The apparatus used for this purpose have been the viscometer of Engler and the septometer, both of which have found extended application. To these valuable, yet always expensive forms of apparatus, I have recently added the "Fluidometer," devised by me and manufactured by the firm of Max Kaehler and Martini, Berlin. I have communicated a description of the same to the Pharmaceutical Society of Berlin.<sup>1</sup> The apparatus possesses besides its inexpensiveness, other merits, chief among which is this, that by means of a simple compression bulb the liquid can be forced back and used for repeated determinations. The apparatus consists of a U formed capillary tube, both of whose limbs are enlarged and divided in such a manner that one arm holds ten cc. and the other two cc. liquid. According to the laws of communicating tubes the liquid flows from the wide limb through the capillary into the smaller limb, which is placed somewhat lower. The viscosity is calculated from the time which is required for the liquid to flow from the first division to the last upper division. There is no danger of error arising from evaporation or contamination with foreign substances in repeating the experiments, and, furthermore, the apparatus is easily and quickly cleaned.

According to the researches of Graham, in 1861,<sup>2</sup> confirmed by those of Pribram and Handl,<sup>3</sup> and by those of Gartenmeister,<sup>4</sup> it was found that the viscosity of a liquid increased with

<sup>1</sup> *Ber. d. Phys. Ges.*, Berlin, 1891, 342.

<sup>2</sup> *Ann. Chem.* (Liebig), 123, 90.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Ztschr. phys. chem.*, 6, 524.

the molecular weight, and the correctness of this law is evident from the following table :

Fatty acids.	Molecular weight.	Pribram and Handl.					Gartenmeister.
		Specific gravity at 20° C.	Boiling-point.	Specific viscosity at 10° C.	Specific viscosity at 30° C.	Specific viscosity at 50° C.	
Propionic acid.....	74	0.9929	140.7	70.3	51.5	49.9	—0.1128
Butyric acid .....	88	0.9580	163.0	110.2	77.4	57.6	—0.1634
Valerianic acid.....	102	0.9386	184.0	152.4	103.3	71.5	—0.2279
Capronic acid.....	116	0.9279	199.7	222.2	139.7	97.8	—0.3263
Heptylic acid .....	130	0.9163	223.0	....	....	....	—0.4440
Octylic acid.....	144	0.9115	237.0	....	....	....	—0.5860
Nonylic acid.....	158	0.9053	253.0	....	....	....	—0.8480

Butter-fat differs from other animal fats in that it contains besides the glycerides of the higher fatty acids, a large amount of the glycerides of butyric, capronic, caprylic, and caprinic acids, and according to the investigations of Duclaux<sup>1</sup> the probable mean composition of butter-fat is:

Palmitin, stearin, olein, } Traces of myristin butin }	91.5 per cent.
Butyrin .....	4.2 "
Capronin .....	2.5 "
Caprylin, caprinin, laurin (traces).....	1.8 "

100.0

It appears therefore that mangarin consists of the glycerides of palmitic, stearic, and oleic acids only. If we compare the molecular weights of the constituents, it follows that the molecular weights of the glycerides of the higher fatty acids are much higher (806–890) than those of the glycerides in natural butter (302–470). The molecular weight determinations of Gaselli and Carcano<sup>2</sup> showed that the molecular weight of pure butter lies between 696–715 while that of margarin lies between 780–883. The fact that molecular weight stands in close relationship with viscosity was confirmed by Killing,<sup>3</sup> although it is known that

<sup>1</sup> Fleischman, *Lehrbuch der Milchwirtschaft*, Bremen, 1893, 30.

<sup>2</sup> Centrbl. Agr. Chem., 1894, 838.

<sup>3</sup> *Ztschr. Angew. Chem.*, 1894, 643.

different samples of margarin show variable values, which could appreciably influence the results in the calculations.

Since it has been demonstrated by the work of Traube<sup>1</sup> that the relation between molecular weight and viscosity is not affected by solvents, I used in my "Fluidometer" a solution of the melted fat in chloroform, merely to avoid the difficult operation of maintaining the melting-point temperature of the fat and I did not lose sight of the fact that the viscosity of the solvent had to be taken into account. Chloroform was used, samples of which from different sources, required, in the mean, 20.04 seconds at 20° C. for efflux. The time of transmission of the solvent is set at 100 and the calculations for solutions are based upon this. From a large number of results I present the following average :

Viscosity value for pure butter	344.30	Time, 68.8
" " " margarin	373.20	" 77.4

Killings' investigations show further that with the one exception of cacao-fat, whose viscosity value falls below that of pure butter-fat, the values for vegetable fats, used by margarin manufacturers are decidedly higher.

Since, however, mixtures can be made whose values approximate that of butter-fat, the Reichert-Meissl method must be resorted to in order to detect the fraud.

A longer or shorter period of standing of the fat solution does not influence the result, whereas every degree of temperature above 20° C. decreases the time of efflux by 1.45 seconds. On the other hand, a decreasing temperature naturally has a retarding influence which averages 1.43 seconds for every degree. The determination of the exact amount of margarin added to butter when the amount of the former is small, cannot be expected of this method, but a largely adulterated sample is easily detected. From the above the following conclusions may be drawn :

1. The viscosity of butter-fat, in chloroform solution, as well as in the pure state, is always decidedly smaller than that of margarin or its solution of equal amount.
2. While the viscosities of different samples of butter show

<sup>1</sup> Berliner, Ber., 1886, 871.



relatively small differences, samples of margarin from various sources, show much larger differences.

3. The viscosimetric determination can yield as good service in distinguishing butter-fat from margarin as any other physical method. The amount of margarin added to butter may also be approximately determined.

4. On account of its easy manipulation, its inexpensiveness, and the small amount of fat necessary, the "Fluidometer" is capable of yielding excellent results, not alone in the hands of experienced chemists, but likewise in those of government inspectors, etc.

### THE EXAMINATION OF LARD FOR IMPURITIES.

BY DAVID WEBBON.

Received June 22, 1895.

IN examining a sample of any material for impurities the analyst must first familiarize himself with the pure substance before he can detect wherein the sample under examination differs. If a definite compound is being dealt with, the problem is an easy one, but if we have an organic substance, which from the very nature of its origin is subject to many variations, the analyst is confronted with a problem of no small magnitude, and this is very true in regard to the accurate analysis of commercial lard, which is the fat rendered from various parts of the freshly slaughtered swine. Hogs being omniverous animals, it is reasonable to suppose that the fat will vary in accordance with the feed. It is a well-known fact that the lard from hogs which have been allowed to run in the woods and fatten on nuts of various sorts, preserves in a marked degree certain properties of the nut oils, and is much softer, containing more oil than that made from corn-fed hogs. That animals under proper conditions absorb food directly and deposit the same more or less unaltered in their tissues, seems to have been proven by experiments made some years ago at the Munich Physiological Institute.

That the fat varies greatly in different parts of the same animal has been demonstrated by various observers<sup>1</sup> as well as the writer.

<sup>1</sup> Wiley: Bulletin 13, Part IV, U. S. Dept. of Agr.; R. T. Thomson and H. Ballantyne; *J. Soc. Chem. Ind.* 9, 589, (590).

E. Spaeth<sup>1</sup> gives table of analytical data showing variations between back, kidney, and intestinal fat, taken from eight different hogs, of different ages. His results show considerable difference between the different animals.

The modes of rendering make considerable differences in the character of the fat. The comparatively low temperature used in kettle-rendering produces a fat of quite different analytical nature from that produced by treatment under high steam pressure in a closed rendering tank (*autoclave*). As most American lard is prepared by this latter method, this fact must be well borne in mind in interpreting analytical results.

Time is an important factor in determining the condition of a lard. A lard several months old will give analytical data which if compared with those of a fresh sample, would indicate adulteration.

The lard analyst who knows nothing of the history of a sample, and without such experience as will enable him to judge by the senses what sort of lard he is dealing with, is extremely liable to misinterpret analytical results and fall into grievous errors.

The methods used for the detection of cottonseed-oil in lard depend upon specific color reaction with different reagents, different physical properties of the fats, and the differences between the fluid portion ("olein") of the lard and that of the cotton oil.

Considering these tests in their order, we will first consider the reaction with silver nitrate, commonly known as the "*Bechi Test*."

Cottonseed-oil when treated with an alcoholic solution of silver nitrate reduces the salt with formation of a brick-red or deep green color and deposition of metallic silver, while pure lard under like conditions should give little or no coloration and no metallic silver. The test has been applied in various ways by different chemists, but the writer has obtained the most satisfactory results by operating according to direction laid down by Dr. C. B. Dudley, in the Penn. R. R. specification for lard oil about six years ago. The solution used is made up with two grams silver nitrate, 200 cc. alcohol, and forty cc. ether. After expo-

<sup>1</sup> *Ztschr. Angew. Chem.* 1893, 133-136; also abstract in *Journal of the Society of Chemical Industry*, 12, 608.

sure to sunlight, till reaction ceases, the solution is decanted or filtered into a dark bottle.

In testing, ten grams of melted lard and five cc. of the solution are well stirred together on the water-bath at  $100^{\circ}$  C. for fifteen minutes, at the end of which time most of the alcohol will have passed off. With pure lard there should be no coloration, while in the presence of cottonseed-oil the depth of color varies according to the amount and character of the oil, and a metallic mirror is deposited on the surface of the liquid fat.

Applying the test, in the manner described, to samples of steam lard known to be pure, and representing many thousand tierces, the writer found that more or less coloration of a purple tint was the rule rather than the exception. Believing that this apparent reduction was due to organic matter of a reducing nature held in the lard as a result of the process of rendering, the experiment was tried of washing the lard with a two per cent. solution of nitric acid. For this purpose about fifty grams of melted lard in a flask are shaken up with twenty-five cc. of the diluted acid, and after allowing to settle on the water- or steam-bath, the acid water is removed and the lard washed once with fifty cc. of hot distilled water. After settling till clear, ten cc. of the lard are pipetted off and the test made as described. In nineteen cases out of twenty, pure steam lard after this treatment will give no reduction whatever or suspicion of reduction, the fat remaining colorless at the end of fifteen minutes, whereas the reducing matter of cotton oil being unaffected by this treatment would give an unmasked reaction with the silver nitrate. While in the majority of cases the above treatment is all that is necessary to remove accidental reducing matters, we occasionally meet lards which have been treated at very high temperature and for a long time, which show as a result a slightly higher than normal per cent of free acid (normal is four-tenths to one per cent) and contain decomposition products of the animal fiber which have a very strong reducing action on our silver solution. Such samples must be first washed with diluted caustic soda solution and distilled water, and afterward with the nitric acid, before any definite conclusion can be drawn from the results of applying the silver nitrate test.

The condemnation of a sample of lard which gives a coloration with silver nitrate, without first purifying the fat as indicated, would be as absurd as it would be unjust, yet many good analysts have been known to do this very thing.

Dr. Ernest Millau applies the silver nitrate to the freshly separated fatty acids, but insists most forcibly on a preliminary preparation of the fat for analysis by a purification somewhat similar to the one outlined above. (See pamphlet<sup>1</sup> published by Ministère de L'Agriculture.)

Exception is taken to the silver nitrate test by various writers because of the misleading reaction obtained with lard improperly prepared for analysis, and also because cotton oil can be refined with oxidizing agents and the use of very high temperatures in such a measure as to destroy the specific reducing agent. Also very old oil will sometimes refuse to give any reduction. If such an oil were mixed with lard, it goes without saying that no reduction would not necessarily indicate pure lard, but the writer can say, as a result of several years' experience, that he has never run across any sample of oil failing to give the reaction which would be suitable to use in the preparation of an edible fat. If a lard containing cotton oil should become so old that the oil should lose its reducing power, the lard would be fit only for the soap-kettle.

The preponderance of evidence seems to be in favor of the silver nitrate test as being the best single test which has yet been brought forward for the detection of cotton oil in lard. When properly applied it is the most reliable for detecting small quantities.

The phosphomolybdic acid test, otherwise known as the Welmans test, first described in the *Pharm. Zeit.*, 1891, 36, 798, has been highly recommended by several writers, of late, as of value for the detection of vegetable oils in lard. Among them may be mentioned Rupp, Wimmer, Mansfield, and Goske, while H. Schweitzer and E. Lungwitz<sup>2</sup> state that they have found the test one of great value.

<sup>1</sup> Analyse Chimique des Matières Grasses Agricoles, par Ernest Millau, Directeur de Laboratoire d'Essais Technique de Marseilles.

<sup>2</sup> *J. Soc. Chem. Ind.*, 614, June 1894.

J. Lewkowitsch<sup>1</sup> says as the results of a series of careful experiments: "Welman's reaction can therefore be admitted as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Samelson<sup>2</sup> concludes that the test is of no value and that the iodine figure is the only reliable test for the detection of cottonseed oil in lard. He bases the assumption on the fact that he found six samples of American lard with iodine numbers of 64.7 to 67.2, which were higher than any he had ever found recorded, whence he concluded that cotton oil must be present though not shown by the test.

George F. Tennille<sup>3</sup> publishes a very exhaustive paper on this test, and concludes that "the phosphomolybdic test may be considered to be of slight analytical value, and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cotton seed or other vegetable oils in lards." The writer has tried the test and arrived at the same conclusions.

*Sulphuric Acid Test.*—The color produced by the action of sulphuric acid on cottonseed-oil in a mixture with lard is often a good qualitative indication, but it so frequently happens that pure lards prepared under certain conditions will give similar coloration, that results must be taken with extreme caution, and in many cases had better not be taken at all.

Dr. J. Lewkowitsch<sup>4</sup> concludes: "The sulphuric acid color test may therefore only be used for purposes of preliminary information, and even then its indications should be interpreted with the greatest caution."

#### PHYSICAL TESTS.

*Specific Gravity.*—Lard freshly rendered in the writer's laboratory showed at  $\frac{99}{15}^{\circ}$  C. a specific gravity of 0.8600 to 0.8610, while old samples of known purity have been observed running as high as 0.8620, while we have on record one specimen which

<sup>1</sup> *J. Soc. Chem. Ind.*, 617, June 1894.

<sup>2</sup> *Ztschr. anal. Chem.*, 189, 1894.

<sup>3</sup> This Journal, 17, 33.

<sup>4</sup> Contributions to the Analysis of Fats, IV, Color Reaction, *J. Soc. Chem. Ind.*, 617, June, 1894.

ran as high as 0.8640, and gave no indication of cotton oil by other tests. The lard was nearly a year old and had been stored in tierces. Cottonseed-oil shows under like conditions 0.8683. With fresh lard as a standard we would have a difference between lard and cotton oil of 0.0083. The lard cited would therefore show  $\frac{0.0040}{0.0083}$  or forty-eight per cent. of cotton oil, which shows the test to give preposterous results when working on old lards. It is of use in obtaining the proportionate components of a mixture when the specific gravities of the identical fats used in preparing the mixture are known.

*Refraction Index.*—As this depends to a great extent on the relative amounts of olein and stearin and palmitin present, it is quite evident that two samples of lard containing these ingredients in different proportions would show different indices. Wiley has published a large number of refraction indices in Part IV, Bulletin 13, Dept. of Agriculture, 1889, Lard and its adulterations. In table 18, he gives the results of analysis of six samples of Prime Steam lard drawn by C. H. Mixer, the official inspector of the board of trade in Chicago, and accompanied by his affidavit. The lards were of unquestioned purity yet their indices varied from 1.4911 to 1.4675, which shows that the refraction index is little better than specific gravity as a test *per se*.

*Melting-point.*—Any one who has experimented much with the melting-points of lard and lard compounds will, it is believed, readily agree that no suitable method has yet been proposed which will give analytical indications of any value except in cases of large admixtures of beef fat. This determination depends so largely on the manner of cooling the fat and the time elapsing after the cooling that it is of no value whatever as an indication of small adulteration.

*Crystallizing-point of the Neutral Fat.*—The observation of the manner of crystallizing on cooling of the melted fat gives valuable indication regarding the presence of beef fat.

H. Schweitzer and E. Lungwitz,<sup>1</sup> give their mode of procedure and results obtained with it. They rely on the test to a

<sup>1</sup> Commercial Analysis of Lard, *J. Soc. Chem. Ind.*, June, 1894, 614, and July, 1894, 709.

considerable extent for the detection of beef fat. Amthor and Zink<sup>1</sup> use this method among others.

The writer has derived very useful indications respecting the proportion of beef fat present in a mixture, by working in a somewhat different manner. As a rule pure lards chill below 30° before showing turbidity, while if beef fat is present crystallization begins at higher temperatures according to the amount present. A lard containing ten per cent. of beef stearin will cloud at a higher temperature than pure lard stearin.

Microscopical examination of the fat crystals deposited from ether is of value for the identification of beef fat when present in large enough amount. When only small amounts of oleostearine are present the test is not as conclusive as the cooling test, unless recrystallization is resorted to.

*Crystallization-point of the Fatty Acids.*— This method, first proposed by Dalican, has for a long time been considered a valuable criterion and is a very useful factor in passing upon the purity of a lard.

The crystallization-point depends upon the relative amounts of solid and fluid acids present, being higher of course in proportion to the increase in the former, but unfortunately the thermometer readings are not in exact ratio to the amounts added.

As the relative amounts of the fluid and solid acids vary in different parts of the same animal it is quite evident that pure lards will show quite different points of crystallization, according to the portion of the animal from which they have been prepared, and also according to the individual, as shown by the results on lards rendered in the U. S. Agricultural Laboratory in Washington and in the writer's laboratory in Chicago some years since.

Part of hog.	According to	
	Wiley.	Wesson.
Head .....	36.6	35.4
Intestine .....	42.7	41.2
Leaf .....	41.3	41.5
Back and sides .....	...	39.7
Belly .....	...	39.7
Foot <sup>2</sup> .....	32.1	...

<sup>1</sup> *Ztschr. Anal. Chem.*, 1892, 584 to 537.

<sup>2</sup> This sample was prepared by a packer but well authenticated.

The crystallization-point of Prime Steam lard or the lard of commerce, varies from 35.5 to 38. The majority of receipts during the past year have shown an average to 36.5, which would indicate that more of the softer parts of the hog are now used than formerly, when the average was one degree higher.

Lard oil has a crystallization-point of  $31^{\circ}$ – $32^{\circ}$ , while well pressed lard stearin should show not less than  $43.5^{\circ}$ .

Considering the wide range in crystallization-point of pure lard, we can only regard the test as a corroborative one, and useful in connection with others in passing upon the purity of a lard, but of little value in proving presence of small amounts of either cotton oil or beef fat.

#### IODINE ABSORPTION.

As the amount of iodine absorbed by a fat depends upon the chemical nature and quantity of the fluid acids present it is evident that in the case of lards it is impossible to draw sharp conclusions, for the softer the lard the more iodine absorbed and conversely. If a standard for purity of lard should be established saying that the correct absorption should be a certain figure, there would be little trouble for the adulterator to make a mixture of cotton oil and beef fat which would fully meet the requirements, and thus make the iodine number prove nothing so far as purity of a lard is concerned. An example or two will make this apparent.

	Iodine number.		
Cotton oil.....	108	10 parts.	10.80
Oleostearin .....	21	10 "	2.10
Steam lard.....	64.5	80 "	51.80
Mixture has iodine number.....			64.50

and contains twenty per cent. of adulteration. The number 64.5 is very near the average for Prime Steam lard and well within limits. Another case would be that of a mixture of intestinal lard testing 52 and cottonseed-oil testing 108, which would contain twenty-five per cent. of the latter and still test 65, while with twenty per cent. cotton-oil the sample would have an absorption of but 63.

In our first example the Dalican temperature of crystallization would be raised a little above normal by the oleostearin, while



in the second instance it would be about normal for pure lard. By normal we mean the temperature of crystallization corresponding to the amount of fluid acid indicated by the iodine number.

Besides the variations caused by the fat being taken from different parts of the hog, we have the difference in individual animals, caused by difference in feed. For instance, Wiley,<sup>1</sup> found on testing the lard rendered in his laboratory from different parts of the same animal, figures which differ considerably from the writer's, as shown in the following table :

Portions of animal.	Wiley.		Wesson.	
	Iodine No.	Point of crystallization.	Iodine No.	Point of crystallization.
Head.....	85.03	36.6	60.35	35.4
Intestine .....	57.34	42.7	52.14	41.2
Leaf.....	62.55	41.3	56.88	41.5
Back and sides...	...	...	57.41	39.7
Belly.....	....	...	58.82	37.7

The results would seem to indicate that one of these hogs judged by the others must have been sadly adulterated. In the writer's opinion, the animal operated on by Wiley, which was purchased in Washington, was very likely one which had gathered a portion of its adipose in the woods of Virginia and adulterated its fat with the oils from beechnuts and acorns, while the writer's hog was a plain, every day Western corn-fed specimen, such as generally comes to the Chicago packers.

The crystallization-points would certainly indicate that considerable differences in the character of the oleins must be the cause of the great differences in the iodine numbers.

To observe the effects of age on samples, those of the writer cited above were tested again after three months standing in the laboratory at from 20° to 30° C., with the following results :

Head.....	63.64
Intestine .....	58.05
Leaf .....	61.02
Back and sides .....	60.50
Belly.....	63.95

Comparing these figures with those obtained on the fresh samples, which, if considered a standard of purity, would lead us to the conclusion that time had been adding some cotton oil. In

<sup>1</sup> Lard and Adulteration Bulletin 13, Pt. IV, U. S. Dept. of Agriculture.

the case of the leaf lard the quantity would appear to be eight per cent.

That age acts in a similar manner on steam rendered lard we can see no reason to doubt.

As a rule the iodine numbers of steam lards run considerably higher than most of the published results on lards.

The iodine numbers of prime steam lard range as follows :

Sample.	Crystallization-point.	Iodine number.	Remarks.
5662.....	39.30	61.95	Wiley : Lard and Adulterations; samples drawn and sworn to by C. H. Mixer, the official inspector at Chicago.
5663.....	38.05	63.82	
5664.....	....	60.34	
5665.....	....	65.12	
5666.....	39.10	60.85	

Sample.	Crystallization-point.	Iodine number.	Remarks.
1.....	36.3	67.22	Lard from 400 tierces and different packers.
2.....	36.0	65.25	
3.....	36.3	69.06	
4.....	36.5	69.26	Age of samples, six to twelve months.
5.....	35.6	67.30	
6.....	37.0	65.31	All samples prime merchantable lard, and unquestionably pure. Tests made in our laboratory.
7.....	37.3	64.31	
8.....	35.0	68.48	

L. E. Spaeth<sup>1</sup> gives results on fats from different parts of eight different hogs and draws the conclusion that a lard must not be considered adulterated merely because its iodine number surpasses sixty. Spaeth's results are :

Age of hog.	Iodine number of fat from		
	Back.	Kidney.	Intestines.
Two years.....	63.25	61.15	62.90
Six to eight months.....	62.95	49.35	57.25
Ten months.....	55.50	55.88	50.60
Six months.....	60.10	55.80	52.30
Five to six months.....	57.08	50.20	51.75
Six to seven months.....	63.61	52.35	49.85
Ten months.....	60.95	46.60	47.60
Six to seven months.....	61.20	51.50	52.85
Mean.....	60.58	52.60	53.10

The above results are especially instructive as showing the great difference which exists between different animals as well as different parts of the same animal.

<sup>1</sup> *Ztschr. Angew. Chem.* 1893, 133-136.

As commercial lard is nowadays made largely from heads, back, and side fat, it is easy to account for the high iodine absorption of prime steam lards.

#### IODINE NUMBER OF THE FLUID ACIDS.

As the fluid acids are the portion of the fat which absorb the iodine, and as the amount of fluid acids present in the fat determine its absorption, which also varies with the nature of the fluid acids present, it follows that the truly scientific method of analyzing a lard is to first determine the percentage of fluid acids present, and then from the iodine number of the fluid acids calculate the proportion of lard and cotton oil present.

This system of analysis was first published by Muter.<sup>1</sup> His process consists in precipitating the lead salts from a neutral solution, extracting the oleate with ether, decomposing the lead soap in the solution with dilute acid, determining the amount of oleic acid present by titrating a measured portion with standard alkali, and then determining the iodine number, using half a gram of the fluid acids under standard conditions. The process though tedious, gives very satisfactory results. Messrs. Muter and DeKoningh published some of the results of the process in the *Analyst*, Feb. 1890. They obtain for the fluid acids of tallow, 90; for lard, 93-94; while for cotton oil, 135.

N. J. Lane<sup>2</sup> reviews Dr. Muter's method, and describes an improvement which gives the results in much shorter time. His results, which were obtained in our laboratory, were as follows:

	Fluid Acids. Per cent.	Iodine number of same.	Hübl number of fat.	Saponi- fication equiva- lent.	Crystalli- zation- point of fatty acids.
Cottonseed stearin .....	68.05	141.09	99.3	288.21	36.6
Summer yellow cotton oil	75.16	141.96	108.36	397.51	32.4
Winter yellow cotton oil..	77.64	143.49	110.96	296.27	30.4
Cotton oil, Columbia, S. C.	76.73	141.97	108.95	284.75	33.8
Cotton oil, New Orleans..	76.67	140.59	109.23	288.94	33.4
Steam lard, ave'ge sample	64.15	99.48	64.96	287.85	37.4
Corn oil (maize oil).....	83.97	144.40	121.7	.....	....
Arachide oil.....	79.84	114.00	93.55	.....	....

In studying the above table it will be noted in the case of cot-

<sup>1</sup> *Analyst* 1889.

<sup>2</sup> This JOURNAL, 15, 110.

ton oil, that whatever variation there may be in the other constants, the iodine number of the fluid acids shows comparatively little variation.

The sample of steam lard mentioned was a composite sample of a number of lots of known purity, representing the article as made at that time.

Wallenstein and Finck<sup>1</sup> work with a modification of the Muter method, which guards more fully against oxidation of the fluid acids by contact with air.

They say: "In deciding qualitatively as to the purity of a fat it may be assumed that below the limit of ninety-six (iodine number of fluid acids) there is no admixture of vegetable oil (except it be cocoanut oil, which is however revealed by the saponification number of the sample). *Between ninety-six and 105 much depends on the origin of the fat.* For instance, Central European lards show ninety-three to ninety-six, while American lards vary between 103 and 106, and additional confirmation by Welman's or Bechi's test will be required to form a decisive opinion."

Results obtained are as follows:

	Iodine number of fluid fatty acids.	Iodine number of Glycerides.
Berlin ox tallow .....	92.2	38.3
Australian tallow .....	92.4	45.2
Hungarian mutton tallow.....	92.7	38.6
American western steam lard.....	104.5	65.4
Berlin hogs' lard.....	96.6	52.7
Hungarian hogs' fat.....	96.2	60.4
Viennese hogs' fat .....	95.2	60.9
Roumanian hogs' fat.....	96.0	59.5
White American cottonseed-oil....	147.5	108.0
Yellow American cottonseed-oil...	147.3	107.8
Yellow Egyptian cottonseed-oil...	148.2	108.0
White English cottonseed-oil.....	146.8	106.5
White German cottonseed-oil .....	147.1	107.1
Yellow Peruvian cottonseed-oil....	147.8	106.8
Maize oil .....	140.7	122.0
Arachis oil.....	128.5	98.5

The above results agree fairly well with Lane's, and are another contribution to the variation of hog fats. The authors attribute the high iodine absorption of the American lard to the

<sup>1</sup> *Chem. Ztg.* 12, 1189-1191; also *J. Soc. Chem. Ind.* Jan. 31, 1895, 78.

difference in feeding methods pursued in America and Europe. They are no doubt right, though the mode of rendering also differs.

At the present time the writer is aware of no method of analysis approaching the modified method of Muter for accuracy, and invariably applies it in doubtful cases.

G. Halphen<sup>1</sup> gives results of a method of separating the fluid and solid fatty acids based on difference in solubility of zinc salts in carbon bisulphide. Their results show that very imperfect separations are obtained and the process has little practical utility. The writer tried the same method in 1888, using gasoline, and obtained better but not satisfactory results.

In conclusion, I would say that working with the best analytical methods at our command, unless the origin of samples is known, the analyst is frequently at a loss to interpret results, in much the same manner as in passing upon a potable water of unknown history, and often when we see the self-confident manner in which small percentages of cotton oil are announced on very questionable data, we feel like exclaiming with the poet,

"Fools rush in where angels fear to tread."

March 12, 1895.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 7.]

## THE ACTION OF HALOID ACIDS IN GAS FORM UPON THE SALTS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND FRED. L. MEYER.

Received May 3, 1895.

**A**FTER observing the conduct of salts of the acids of elements of Group V toward hydrochloric acid gas, it was but natural that we should, with some interest, note the results arising when the other haloid acids, in gas form, were substituted for hydrogen chloride. It was useless to predict what might occur, and, therefore, the slight variations from preconceived notions were in no wise surprising. Taking up the study of the haloid acids and the various salts in the order of increasing molecular magnitude, we began with

<sup>1</sup>*J. de Pharm. et Chim.*, 30, 241-247, 1894.

#### 1. THE ACTION OF HYDROFLUORIC ACID GAS UPON SODIUM NITRATE.

The salt was exposed to the action of the gas in a platinum boat, carried in an iron tube. The temperature at which the reaction was conducted did not exceed  $250^{\circ}$  C. Not more than twenty minutes were allowed, or required, for the change which, from the analytical result given below, is evidently complete.

*Experiment.*—0.1052 gram of sodium nitrate gave 0.0530 gram of sodium fluoride, instead of 0.0520 gram, the theoretical amount.

A second trial gave a similar quantitative result.

#### 2. THE ACTION OF HYDROFLUORIC ACID UPON PHOSPHATES.

The gaseous acid expelled nothing from sodium pyrophosphate. The boat contents sustained no loss in weight. The water in the receiver gave no evidence of the presence of phosphorus when tested for it.

#### 3. HYDROFLUORIC ACID AND VANADATES.

Sodium vanadate, thoroughly dried, was heated to  $250^{\circ}$  C., for one-half hour in an atmosphere of the acid vapor. Vanadium was found both in the receiver and in the boat. Upon repeating the experiment, increasing the temperature, and continuing the action of the acid vapor through an hour, about one-half of the vanadic acid was volatilized.

#### 4. HYDROFLUORIC ACID AND ARSENATES.

In these trials sodium pyroarsenate was heated to about  $400^{\circ}$  C., while exposed to a brisk current of the acid vapors.

*Experiment 1.*—0.1893 gram of sodium pyroarsenate was used. When the boat-contents were examined 0.0872 gram of the pyro-salt was found unvolatilized.

*Experiment 2.*—0.2015 gram was treated in the same manner, with practically the same result. The volatilization, therefore, of the arsenic compound must be considered as incomplete.

To summarize, nitrates are entirely converted into fluorides by the vapors of hydrofluoric acid; with vanadates and arsenates the conversion is incomplete, while phosphates remain intact.

## 1. HYDROBROMIC ACID AND NITRATES.

Apparently no change occurs when these compounds are brought together in the cold. When gently heated aqueous vapor and bromine appear. In the course of half an hour the conversion into bromide is finished.

*Experiment.*—0.1887 gram of sodium nitrate gave 0.2286 gram of sodium bromide, instead of the theoretical 0.2273 gram.

## 2. HYDROBROMIC ACID AND PHOSPHATES.

Not even traces of phosphoric acid were expelled on heating sodium pyrophosphate in an atmosphere of hydrobromic acid.

## 3. HYDROBROMIC ACID AND VANADATES.

Sodium vanadate was acted upon in the cold. It became brown in color, and when the temperature was raised to almost 300° C., vapors escaped and condensed to an oily, reddish liquid beyond the heated portion of the tube. By the continued action of the acid this liquid acquired a green color, and small, green-colored crystals appeared. After the lapse of half an hour the liquid had completely solidified to a mass of radiating needles, having a beautiful green color. Several analyses of this compound showed the presence of 59.40 per cent. bromine and 14.65 per cent. vanadium, which would closely approximate the formula  $V_2O_5 \cdot Br_3 \cdot 3HBr \cdot 7H_2O$ , requiring 58.91 per cent. bromine and 15.02 per cent. vanadium. That such an oxybromide is not improbable may be inferred from the fact that Ditte (*Comptes rendus*, 102, 1310) prepared the compound  $V_2O_5 \cdot Br_2 \cdot 2HBr \cdot 7H_2O$ , by boiling vanadic oxide ( $V_2O_5$ ) with hydrobromic acid. It required 53.51 per cent. bromine and 17.06 per cent. vanadium. The conversion into bromide was not complete.

## 4. HYDROBROMIC ACID AND ARSENATES.

Quite a distinct reaction was evident with pure, dry, sodium pyroarsenate even in the cold. The salt assumed a dark-grey color. When a gentle heat was applied to it vapors were expelled; these condensed in the anterior portion of the tube to a pale-yellow, oily liquid, soluble in water. The temperature at which the reaction was carried out did not exceed 300° C. The boat contained pure sodium bromide.

*Experiment 1.*—0.5440 gram of pyroarsenate gave 0.6335 gram of sodium bromide, instead of 0.6331 gram, the theoretical quantity.

*Experiment 2.*—0.4277 gram of pyrophosphate gave 0.4984 gram of sodium bromide, while theory requires 0.4981 gram.

With this complete, quantitative expulsion of arsenic, and the non-volatilization of phosphoric acid before us, we next proceeded to the separation of the two acids, both being present as sodium pyro-salts.

*Experiment 3.*—0.1572 gram of sodium pyroarsenate and 0.1897 gram of sodium pyrophosphate were mixed and gently heated in hydrobromic acid gas. The phosphate remaining in the boat, when determined and calculated into pyro-salt, equaled 0.1903 gram. As it was free from arsenic, we did not estimate the arsenic contained in the receiver.

Through both hydrobromic acid and hydrochloric acid vapors, acting upon a mixture of arsenates and phosphates, a separation of the two acids may be effected.

The succeeding experiments relate to the conduct of nitrates, arsenates, and phosphates toward hydriodic acid gas. This was prepared by dropping water upon a mixture of amorphous phosphorus and iodine. It was carefully dried before it came in contact with the salts.

#### I. HYDRIODIC ACID AND NITRATES.

Sodium nitrate was changed by the gas into iodide. One approximate result may be given :

0.1039 gram of sodium nitrate gave 0.1886 gram of sodium iodide, instead of the theoretical 0.1833 gram.

Not one experiment could be completed, since explosions of considerable violence invariably occurred. A dark sublimate, apparently iodine, appeared in the tube, and after the lapse of a quarter of an hour a flash of fire ran through the tube, accompanied by a loud report. Not succeeding in finding a method to prevent this, further work was abandoned. These explosions



were doubtless due to the production of some unstable derivative of nitrogen and iodine.

Phosphates were not altered by contact with hydriodic acid gas.

## 2. HYDRIODIC ACID AND ARSENATES.

Sodium pyroarsenate was employed. In the cold the acid gas produced a change. Thus, 0.1592 gram of pyro-salt gave 0.2672 gram of sodium iodide, instead of 0.2689 gram. The arsenic volatilized, determined, and calculated into pyro-salt gave 0.1583 gram instead of 0.1592 gram. As explosions occurred in all the trials made we concluded to abandon the study.

It may not be uninteresting to present a scheme of the elements, composing Group V of the periodic system,

Nitrogen	Phosphorus	Arsenic	Antimony	——	Bismuth
14	31	75	120	164?	208
	Vanadium	Columbium	Didymium	Tantalum	
	51	94	142	182,	

and briefly review their deportment so far as known, when acted upon by the gaseous haloids. Nitrogen is fully expelled by all of them from nitrates. Phosphorus, existing as phosphates, apparently is absolutely uninfluenced and remains unaltered in the salts with which experiments were tried. Arsenic is only partially volatilized from arsenates by hydrofluoric acid gas, but is completely removed by any one of the remaining haloid acids. Antimony is fully expelled from antimonates by hydrochloric acid gas. No experiments have been tried with bismuth. Hydrofluoric and hydrobromic acid gas volatilize vanadium in part, while its removal from sodium vanadate by hydrochloric acid gas is complete. We have no knowledge of the action of hydriodic acid. Columbium yields volatile products with both hydrochloric and hydrobromic acid vapors. Didymium has never been subjected to this treatment. Tantalum is but slightly affected by the vapors of hydrochloric acid, although it has long been known that both the oxide of columbium and that of tantalum are volatilized to a marked degree when heated with aqueous hydrofluoric acid.

## SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

By L. DE KONINGH.

Received June 3, 1895.

THE April number of this Journal (289-295) contains a criticism, by Twitchell, of some processes for the separation of solid and liquid fatty acids. Being joint author with Muter of the process referred to on page 290, I wish to make a few observations.

The author states that he carefully carried out Muter's instructions in all important details. I beg to differ from him. We work directly on the fat and not on the fatty acids isolated therefrom. We do not *boil* with ether to dissolve the lead oleate, and after having taken the trouble to expel the ether by means of a current of carbonic acid we do not undo any good this may have done by passing a current of air, but add the Hübl solution directly, as we know the weight of the oleic acid by a previous titration. I feel sure, however, that there is a deal of exaggeration about all this danger of oxidation.

The lead oleate is precipitated as a bulky semi-fused mass which soon solidifies, and if ever so sensitive to oxygen can only be affected very superficially. When dissolving in ether the flask is nearly filled and the little air remaining is practically expelled by ether vapor, so that the few cc. of oxygen left certainly cannot cause a great oxidation. Even on filtering, the air is not likely to act much on a liquid which is always in an active state of evaporation and consequently repels the air. I feel sure that lead stearate and palmitate are insoluble in ether; then when carrying out the separation from the oleate, there soon comes a time when the filtrate no longer colors with ammonium sulphide. The author's suggestion, that it may be more soluble in ether containing lead oleate, is not supported by my own experience. Then Muter and I have stated in the *Analyst*, 15, 49, that the liquid acid from tallow gives practically the iodine figure of pure oleic acid. For lard acid we found, however, ninety-three to ninety-four per cent., and I am pleased to see Twitchell's confirmation of this figure.

As gold alloys containing too little silver cannot be parted by means of nitric acid, so the separation of lead oleate from lead stearate fails if too little of the former is present. I published, two years ago, a short article in the *Chem. News*, **66**, 259, dealing with this subject, and refer to the same.

### ACETIC ACID IN VINEGAR.

BY ALBERT R. LEEDS.

Received May 21., 1895.

RECENTLY, having occasion to determine the acetic acid in many samples of vinegar, I was surprised to find how vague and unsatisfactory are the directions relating to this simple matter in many text-books and manuals for public analysts.

One of the latter recommends that fifty cc. of vinegar should be used and the titration performed with soda, no particular strength or indicator being mentioned. Another, in general terms, calls attention to the fact that only approximate results can be obtained with soda, its acetate having a feeble alkaline reaction. The indicator, in the presence of which it so reacts, is not stated. Sutton's Volumetric Analysis calls attention to the necessity of substituting phenolphthalein for litmus, the acetates of the alkalies and alkaline earths having a perfectly neutral reaction to the former. He further adds that colored vinegars may be so titrated even when highly diluted.

Beginning with twenty-five cc., which I found at once to be much too large a quantity, and using seminormal acid soda as a convenient strength of alkali, I presently reduced the volume of vinegar to ten cc. and finally to five cc. When this was diluted with fifty cc. of water in a white porcelain dish, and phenolphthalein was used as indicator, the end reaction was satisfactory, except in the case of highly colored vinegars. In these it is not sharp. Nor can litmus paper or litmus solution be satisfactorily used with them. Litmus gives not only a lower reading, but lower by a very variable amount in different vinegars. Sixteen samples tested as above described gave percentages ranging from 2.63 per cent. to 5.65 per cent., with a mean of 4.49. A mixture made up of twenty-five cc. of each, gave 4.44 per cent. The color of these samples was white to dark brown.

According to Sutton, Pettenkoffer titrates vinegar with a known excess of baryta and estimates the excess with decinormal nitric or oxalic acid by the help of turmeric paper.

Thinking that baryta might give a sharper reaction, though not discerning any advantage in the use of decinormal oxalic or nitric acid, I used an approximately decinormal baryta solution with phenolphthalein and decinormal hydrochloric acid. The results agreed to 0.01 per cent. with those obtained with soda, and ordinarily the latter would be the more convenient and preferable reagent.

Sutton recommends as a process applicable in all cases and however dark the vinegar may be, the method of C. Mohr, which consists in adding to a known quantity of the vinegar a known excess of barium or calcium carbonate in fine powder. Pure calcium carbonate, he states, is preferable, as it dissolves more readily.

In his excellent manual on "Foods" page 518, Blyth adds: "If absolutely accurate determinations are required, it is best to add an excess of pure calcium carbonate to a known weight; the liquid is boiled, filtered, and the residual carbonate dissolved in slight excess of normal hydrochloric acid and titrated back with soda and cochineal. From the amount of carbonate thus found to have been unacted upon, the total acidity is calculated."

This process failed entirely in my hands; I took fifty cc. of the vinegar and added two and a half grams of pure precipitated calcium carbonate in fine powder. The flask was corked loosely and shaken many times each day during the course of six days, at the end of which time the contents were still acid. Also, the flask was gently heated at intervals some five to six hours in all. The acetic acid still remaining, after filtering off the calcium carbonate, amounted to nine-tenths per cent. The figure calculated from the residual carbonate corresponded to 3.64 per cent., or a total of 4.54 per cent. as against 4.44 per cent., found directly with soda.

Regarding the amount of vinegar as too large and the difficulty as probably due to the slowness with which a very dilute solution of acid decomposed the carbonate towards the end of the reaction, I then treated ten cc. with excess of carbonate for

two hours under a return-condenser. This was somewhat more successful, the liquid containing 0.72 per cent. and the figure calculated from the residual carbonate corresponded to 3.85 per cent.—a total of 4.57 per cent.

The true percentage being thus rendered very doubtful, I then had recourse to another recommended by Blyth. He states, page 517, that the strength may be accurately estimated by distilling 110 cc. until 100 cc. have been drawn over, *i. e.*, ten-elevenths." The 100 cc. will contain eighty per cent. of the entire acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken and the strength found from the following table: "A trial by this method yielded a distillate with specific gravity of 1.055 at 15°, corresponding in the table given to 4.25 per cent.; in one trial, the distillate should by titration, 4.23 per cent., in another, 4.24. Assuming for reasons stated below, that the correct percentage was 4.43, these figures correspond to ninety-six per cent. of the acid instead of eighty.

The method of distillation was then varied in the following manner: Ten cc. were diluted with fifty cc. of water in a small retort the neck of which was inclined upward and then bent downward to join the condenser. The distillation was continued until about two cc. remained in the retort when another fifty cc. of water was added and the distillation repeated—in all four times. The distillates had a faint acetous, mingled with a pronounced hop-like odor, on adding silver nitrate they presently darkened and on standing threw down a black deposit. They contained:

- |    |       |                    |               |      |                     |
|----|-------|--------------------|---------------|------|---------------------|
| 1. | 3.73  | per cent. of acid, | equivalent to | 83.2 | per cent. of total. |
| 2. | 0.54  | "                  | "             | "    | "                   |
| 3. | 0.081 | "                  | "             | "    | "                   |
| 4. | 0.041 | "                  | "             | "    | "                   |

During this long process I had obtained only 4.39 per cent. acid or ninety-nine per cent. of the total.

The distillation was repeated in the same manner, using ten cc. of vinegar and fifty cc. of water in three successive additions, but the vinegar had previously been strongly fortified with phosphoric acid. One trial gave 4.507 per cent. acid, another 4.514.

The distillates gave no reaction for chlorine, and possibly the high figure was due to the presence of a little acetate.

Finally, in order to get rid of the disturbing influence of the coloring matters the following method was adopted. Fifty cc. of vinegar with fifty cc., of water and a drop of phenolphthalein were titrated with decinormal baryta, the latter being added to three cc. in excess, and then followed by five cc. of decinormal sulphuric acid. Whether the precipitates were allowed to settle in the cold or with warming, appeared to make no difference in the results, the coloring-matters being carried down very nicely. In one trial the precipitate was filtered off and thoroughly washed before titrating back with acid: in another, the assay was made up to 100 cc. in a graduate and twenty-five cc. were pipetted off and titrated. The former corresponded to 4.48 per cent., the latter to 4.52 per cent. The bulk of the precipitate was approximately one cc., and making the requisite correction gives us 4.48 for the latter result also.

These figures being higher than those obtained directly, I then went back to the use of turmeric, so highly recommended by Pettenkofer, and obtained 4.43 per cent. With great care in the observation of the first brown ring which forms in the presence of the slightest excess of baryta, when a drop of the titrated solution is brought upon turmeric paper, the end reaction can be detected with certainty. The reading is lower than that with phenolphthalein and may be relied upon even with highly colored vinegars. For ordinary purposes, however, the latter indicator with decinormal soda is adequate.

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### NEW BOOKS.

AN ELEMENTARY COURSE IN EXPERIMENTAL AND ANALYTICAL CHEMISTRY. BY JOHN H. LONG, M.S., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES OF THE SCHOOLS OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. pp. 507. Chicago: E. H. Colegrove & Co.

This book considers three subjects. Part I, covering 275 pages, is devoted to experimental chemistry. The first chapter presents experiments in crystallization, in distillation, and those

that show the difference between physics and chemistry. In the second chapter, oxygen, hydrogen, and their compounds are considered. The halogens and their derivatives constitute the third chapter. At this point elements and compounds, as well as the use of symbols, are discussed. Nitrogen and the atmosphere are the subjects of experimentation in chapter four, while the fifth, sixth, and seventh chapters are occupied by the other frequently occurring non-metals and their derivatives. Seven chapters follow; in them facts relating to the more important metals are presented in simple experiments. Analytical tests follow each metal. Combining weights, the atomic hypothesis, and valency are considered immediately after the metal magnesium. It may be inferred from this that the author advocates first giving to the student an abundance of facts before deducing theories or entering upon a discussion of fundamental principles. This thought is constantly before the reader throughout the entire book. The explanations accompanying the numerous experiments in Part I are clear and to the point. It must be admitted that the author has presented his subject in such a manner that good will result. Part II (twelve chapters) is given to qualitative analysis. The subject-matter is not exhaustive, but here, as in Part I, types are presented to the student. These he works out in detail, being assisted in his efforts by valuable explanatory remarks on the part of the author. Part III considers the elements of volumetric analysis. The examples selected for work are typical and cover a wide field. Recent methods of value have not been overlooked. In this section, as in the two preceding sections, the author has presented all the subject-matter in a very clear style. In short, after careful inspection of the book one lays it down with the conviction that it possesses great merit; it is an excellent book and worthy of commendation.

EDGAR F. SMITH.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS. BY ALFRED J. MOSES AND CHAS. L. PARSONS. pp. 342, with illustrations. New York: D. Van Nostrand Co., 1895.

This work, as indicated in its preface, is mainly intended for use as a text-book. It is divided into four parts: I. Crystallog-

raphy; II. Blowpipe Analysis; III. Descriptive Mineralogy; IV. Determinative Mineralogy.

The authors have given considerable space to crystallography, having devoted about one-fourth of the entire volume to the subject. The text is well written and fully illustrated.

In part II, after a chapter devoted to the apparatus, flame, etc., there is given a detailed description of the "Operations of Blowpipe Analysis," the reagents employed, and the results obtained in the various manipulations. This is followed by a series of "Useful Tests with the Blowpipe" on all of the principal elements. A valuable feature of this last chapter is a list of "Interfering Elements," which follows tests given for each element and in which directions are given for obtaining the proper reactions. The section is concluded by a chapter on "Schemes for Qualitative Blowpipe Analysis."

Part III, on Descriptive Mineralogy, occupies the major part of the book. The two first chapters treat of the physical characters and chemical composition of minerals. While the definitions of terms are clear and concise, they are in a few cases abridged to incompleteness and explanation of the optical and magnetic properties are omitted entirely.

The remaining chapters describe the various minerals under the heads of the elements forming their principal component parts. A distinguishing and most useful feature of this part of the work are the general remarks at the beginning of each chapter concerning the economic uses of most of the important minerals and ores.

The book would be more useful as one of reference, particularly to the analyst, if more attention had been given to the percentage composition. Many minerals have it in full, others only partially, while not a few have the formula only given.

Part IV consists of a number of tables of the usual tests for the rapid determination of minerals.

The arrangement of the book as a whole is excellent, and although the subject matter has been largely condensed, the elimination of less important details has made it much more practical than text books usually are, and it should be found useful to the professional mineralogist and chemist.

H. B. BALDWIN.



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### AMMONIUM PHOSPHOMOLYBDATE AND THE REDUCING ACTION OF ZINC IN THE REDUCTOR.

BY ANDREW A. BLAIR AND J. EDWARD WHITFIELD.

Received August 7, 1895.

**A**MONG the problems presented to the sub-committee on Methods of the International Steel Standards Committee, in the choice of a method for the determination of phosphorus in steel, none seemed more important than those involved in the composition of ammonium phosphomolybdate, and the reducing action of zinc on the molybdic acid of this salt under different conditions. The object of this investigation was to present data for the settlement of this question.

#### COMPOSITION OF AMMONIUM PHOSPHOMOLYBDATE.

In the preparation of ammonium phosphomolybdate the method usually followed was to precipitate the salt by adding a solution of microcosmic salt to a solution of ammonium molybdate in nitric acid; but Doolittle and Eavenson<sup>1</sup> showed that ammonium phosphomolybdate precipitated from a solution containing a large excess of ferric nitrate had essentially the same composition as that obtained by following the usual method of procedure.

In the investigation which we have made, we prepared a number of samples under different conditions and made careful analysis of each as a basis for our work.

<sup>1</sup> This Journal, 16, 234.

*Sample 1.*—Prepared by dissolving twenty grams of steel free from arsenic in nitric acid, adding twenty-five cc. of a saturated solution of microcosmic salt, evaporating to dryness, heating until the ferric nitrate was decomposed, dissolving in hydrochloric acid, diluting, filtering, evaporating to syrupy consistency, and then evaporating three times with excess of nitric acid to remove the hydrochloric acid. The solution was diluted to one liter, heated to about 60° C., and poured into one liter of molybdate solution. The precipitate was allowed to settle, the supernatant liquid was decanted, and the precipitate was washed by decantation with water containing one per cent. of nitric acid and finally filtered, washed, dried, removed from the filter, and heated to 150° C. for five hours.

*Sample 2.*—Prepared by partially neutralizing the first decantation from sample 1, adding twenty-five cc. more of the same microcosmic salt, washing, and drying the precipitate as above.

*Sample 3.*—Prepared by pouring a solution of microcosmic salt acidulated by nitric acid into molybdate solution, washing with water containing one per cent. of nitric acid, and filtering. A portion of this precipitate was dried at 150° C. for eight hours for sample 3.

*Sample 4.*—Prepared by taking a second portion of the precipitate above, washing with ice-water and drying over potassium hydroxide at the ordinary temperature for three months.

*Sample 5.*—Prepared by taking a third portion of the same precipitate, washing again with water containing one per cent. of nitric acid, and drying in the same manner as sample 4.

*Sample 6.*—The same as sample 5, but digested and washed before drying with water containing five per cent. of nitric acid.

*Sample 7.*—The same as sample 5, but digested and washed with water containing ten per cent. of nitric acid.

*Sample 8.*—Prepared by dissolving ferric oxide (obtained by igniting pure ferric oxalate) in hydrochloric acid, adding five per cent. of pure phosphoric anhydride, evaporating off the hydrochloric acid with nitric acid, heating to 80° C., adding an

excess of molybdate solution at 20° C., shaking in a large flask for three minutes and washing with water containing one per cent. of nitric acid. After thorough washing, the precipitate was digested with consecutive portions of water, containing varying amounts of nitric acid and with water containing nitric acid and ammonium nitrate. Then after standing two months with half a liter of water, containing five per cent. of nitric acid, it was filtered, washed with water containing five per cent. of nitric acid, and heated to 100° C. for five hours.

*Sample 9.*—Prepared from the same reagents, and in the same manner as sample 8. Washed by decantation with water containing five per cent. of nitric acid, dried at 100° C. for eight hours.

*Sample 10.*—Prepared and washed in the same manner as sample 9, but dried at 100° for twelve hours.

The methods employed in the analyses of these samples are the usual ones except that for the determination of water, and a general description will be sufficient.

As the salt is very hygroscopic, the samples were in all cases placed in drying tubes with glass stoppers, heated to the temperature indicated, cooled over fused potassium hydroxide, and weighed out by difference.

#### DETERMINATION OF PHOSPHORIC AND MOLYBDIC ACIDS.

About two grams of the salt was weighed out by difference into a beaker, dissolved in twenty-five cc. of ammonia (0.96 sp. gr.) transferred to a carefully calibrated half liter flask and diluted to the mark with water. The solution was thoroughly mixed by pouring it into a dry beaker and back into the flask several times. By means of a pipette, which had been carefully tested against the flask, 100 cc. (containing about four-tenths gram of the salt) was measured into a beaker for the estimation of the molybdic acid, and 200 cc. (containing about eight-tenths gram of the salt) was measured into another beaker for the estimation of the phosphoric acid. To the latter was added, drop by drop, ten cc. of magnesia mixture with constant stir-

ring, then fifty cc. of ammonia and the precipitated ammonium magnesium phosphate was allowed to stand over night. The precipitate was filtered, washed with ammonia water, dissolved on the filter in dilute hydrochloric acid, made slightly alkaline with ammonia, ammonium sulphide added, the solution acidulated with hydrochloric acid and hydrogen sulphide passed through the hot solution for half an hour. The precipitated molybdenum sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide and the ammonium magnesium phosphate reprecipitated as before. This precipitate was filtered off, burned and weighed as magnesium pyrophosphate, and the phosphoric acid and phosphorus calculated in the usual way.

The solution for the determination of molybdic acid was diluted to about three-fourths of a liter with hot water, heated to boiling, slightly acidulated with acetic acid and a boiling solution of lead acetate (containing about three grams of the salt) was added. After boiling for about fifteen minutes the precipitate was allowed to settle, decanted through an asbestos filter on a Gooch crucible, washed thoroughly by decantation with hot water, transferred to the crucible, dried at  $120^{\circ}$  C., and weighed as the mixed lead phosphate and molybdate.

The percentage of the mixed salts was calculated and from this amount was subtracted the percentage of lead phosphate found by multiplying the percentage of phosphorus previously found by 13.086. The difference (lead molybdate) multiplied by 0.39242 gave the percentage of molybdic acid.

#### DETERMINATION OF AMMONIA.

About one and a half to two grams of the salt was weighed out into a funnel inserted in the neck of a fractional distillation flask and washed down into the flask with water. The flask was fitted with a stopper carrying a bulb tube with a glass stopcock. The side tube of the flask was fitted into a glass condenser to the lower end of which was attached one arm of a large bulb U tube containing ten cc. of hydrochloric acid and twenty cc. of water. The other arm of the U tube was fitted with a small calcium chloride tube, containing broken glass moistened with water. Fifty cc. of pure potassium hydroxide (1.27 sp.

gr.) was admitted to the distillation flask through the bulb tube, and the ammonia was distilled over. The contents of the U tube were transferred to a beaker, platinic chloride added, and the ammonia determined in the usual way.

#### DETERMINATION OF WATER.

The determination of water in ammonium phosphomolybdate offered unexpected difficulties. After repeated trials to get satisfactory results by heating the salt with sodium tungstate the following method was adopted :

At the middle point of a tube of hard glass 200 millimeters long, and nineteen millimeters in diameter was fused at right angles a tube thirty-seven millimeters long and nine millimeters in diameter. In the small tube a thermometer was fitted with sheet asbestos. The bulb of the thermometer extended a short distance into the large tube. The tube was placed in a horizontal position across the ring of an iron retort holder, the middle of it being protected by a piece of sheet copper three inches long bent around it, but separated from it by sheet asbestos. The ends of the tube were fitted with perforated corks, one carrying a small glass tube for the passage of dry air, and the other a U tube filled with calcium chloride. A porcelain boat sixty-two millimeters long and twelve millimeters wide was provided to hold the salt.

The stand holding the tube now closed with solid stoppers was placed near the balance case, about two grams of the salt was weighed out by difference into the boat which was immediately placed in the tube, and the latter closed by the corks. It was then placed in position, the perforated corks substituted for the others and a current of dry air passed through while the tube was heated by a Bunsen burner until the thermometer registered  $250^{\circ}$  C. The increase in weight of the calcium chloride tube gave the amount of water.

The only danger apprehended was that of decomposing the salt and liberating its ammonia, but careful experiments made by passing the air over the salt heated to  $250^{\circ}$  C. and into Nessler's solution showed that no trace of ammonia was given off.

The results of the analysis of the samples are as follows :

Sample.	Phosphoric acid.	Molybdic acid.	Ammonium oxide (NH <sub>4</sub> ) <sub>2</sub> O.	Water.	Ratio of Phosphorus to 100 molybdic acid.
	Per cent.	Per cent.	Per cent.	Per cent.	
1	3.79	91.88	3.33	1.02	1.799
2	3.79	91.63	3.39	1.30	1.805
3	3.80	91.67	3.34	1.22	1.810
4	3.59	88.06	3.36	5.02	1.778
5	3.63	89.07	....	....	1.786
6	3.57	86.44	....	....	1.802
7	3.56	86.89	....	....	1.789
8	3.73	91.37	2.64	1.96	1.780
9	3.79	92.33	3.12	0.71	1.790
10	3.81	91.96	3.03	1.17	1.807
Average for the ten samples,					1.7946

These results are sufficient to show remarkable uniformity in the composition of ammonium phosphomolybdate precipitated under varying conditions and may be considered as practically answering the question as to the effect of the presence of ferric nitrate in the solution from which the precipitation is effected.

There are two points worthy of remark in these results. First, the variation in the amounts of water in the different samples, and second, the variation in the amounts of ammonia.

The explanation of the first point is found probably in the temperature of drying, that of the second in the washing of the precipitated salt. Sample 8, which was digested for a long time with dilute nitric acid, had lost most ammonia. This is borne out by the fact that the ammonia can all be destroyed by digestion with aqua regia and phosphomolybdic acid crystallized out from the solution. In this connection the following table of calculated composition compared with results obtained by analysis may be of interest :

## SAMPLE 10.

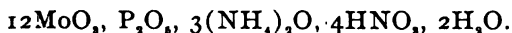
		Theory. Per cent.	Actual determination. Per cent.
24 MoO <sub>3</sub> .....	3456	91.19	91.96
P <sub>2</sub> O <sub>5</sub> .....	142	3.74	3.81
3 (NH <sub>4</sub> ) <sub>2</sub> O .....	156	4.12	3.03
2 H <sub>2</sub> O .....	36	0.95	1.17
	4790	100.00	99.97
Phosphorus ratio .....		1.794	1.807

## SAMPLE 4.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO <sub>3</sub> .....	3456	87.45	88.06
P <sub>2</sub> O <sub>5</sub> .....	142	3.59	3.59
3 (NH <sub>4</sub> ) <sub>2</sub> O .....	156	3.95	3.36
22 H <sub>2</sub> O .....	198	5.01	5.02
	3952	100.00	100.03
Phosphorus ratio .....		1.794	1.778

The last trace of water seems to go off between 150° and 250° C., but the samples having been prepared and analyzed after drying at or below 150° C it was not deemed necessary to prepare the anhydrous salt especially as it is very hygroscopic. In view of the fact that the variation in the ratio of molybdic acid to phosphorus is so small (the average of the ten samples being 1.7946) we may without hesitation adopt the theoretical ratio of 1.794.

Samples 4, 5, 6, and 7 were prepared to test the accuracy of the statement made by Hundeshagen<sup>1</sup> that the precipitated ammonium phosphomolybdate washed with dilute acid and dried in a desiccator over calcium chloride and potassium hydroxide had the composition



Actual tests of these samples made by dissolving weighed amounts in a standard solution of potassium hydroxide and titrating back with standard nitric acid gave the following results:

	Standard alkali required to neutralize one gram of salt.
No. 3 .....	130.53
" 4 .....	119.14
" 5 .....	121.25
" 6 .....	123.59

Sample 7 was unfortunately used up in the preliminary analysis and none remained for this test, but as No. 3 was heated to 150° C., and the others were dried as described above, No. 4 having been washed with water, No. 5 with one per cent. nitric acid, and No. 6 with five per cent. nitric acid the results do not seem to bear out Hundeshagen's statement.

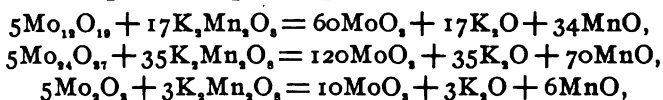
<sup>1</sup> *Chem. News*, 60, 168.

It was hoped also, that the neutralization (Handy's) method might offer some advantages over the reduction method for the determination of phosphorus in steel, but the hygroscopic character of the ammonium phosphomolybdate and the lack of agreement in the results obtained caused us to abandon this part of the investigation.

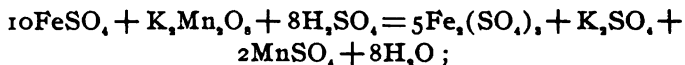
#### THE REDUCTION OF MOLYBDIC ACID BY ZINC.

When a solution of ammonium phosphomolybdate in ammonia is acidulated with sulphuric acid and the molybdic acid is reduced by metallic zinc it was claimed by Werncke that the reduction was not to the form  $\text{Mo}_2\text{O}_3$ , but to  $\text{Mo}_{11}\text{O}_{11}$ . This theory was adopted by Emmerton and has been generally accepted by chemists as the formula to be used in the determination of phosphorus by the reduction method. When Jones' reductor came into general use it was noticed that the green color of the reduced solution was more permanent and the oxidation with potassium permanganate was from this color and not from the port-wine color referred to by Emmerton. Babbitt' claimed that the reduction was to a point between  $\text{Mo}_2\text{O}_3$  and  $\text{Mo}_{11}\text{O}_{11}$ , but Noyes' claimed that the reduction was to  $\text{Mo}_2\text{O}_3$ .

The reactions may be indicated as follows for the subsequent oxidation by potassium permanganate :



then as



or one molecule  $\text{K}_2\text{Mn}_2\text{O}_8$  oxidizes ten molecules of iron to the ferric condition, and we have for the ratio of iron to molybdic acid 100 to 90.756 in the first case, to 88.163 in the second, and to 85.714 in the third.

In other words, we must multiply the value of the permanganate solution in iron by 0.90756, by 0.88163, or by 0.85714 according to the theory we adopt for the reducing action of zinc on the solution of ammonium phosphomolybdate.

<sup>1</sup> *J. Anal. Appl. Chem.* 7, 165.

<sup>2</sup> This Journal, 16, 553.



The differences are certainly too great to be disregarded, and it becomes necessary to decide which theory we must adopt.

We have, therefore, sought to discover in the following experiments, first, what conditions affect the reduction, and secondly, whether the methods in ordinary use are capable of giving uniform results.

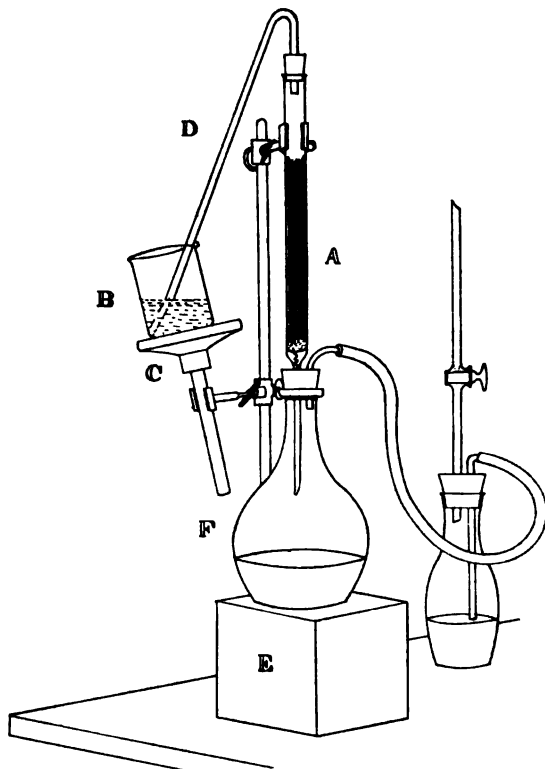
First, sample 10, containing 91.96 per cent. molybdic acid was selected for these experiments and a number of glass stoppered weighing tubes were filled with the carefully ground and dried salt. About two grams of the salt was weighed by difference into a beaker, dissolved in five cc. ammonia (0.96 sp. gr.) washed out into a half liter flask, diluted to the mark with distilled water, mixed by pouring back and forth into a dry beaker, and measured out by means of a twenty-five cc. pipette, carefully tested with the flask into beakers. Twenty cc. ammonia (0.96 sp. gr.) were added, the solution was acidulated with twenty-five cc. sulphuric acid (1-4) and passed through the reductor. The reduced solution was titrated with standard permanganate and the molybdic acid calculated by the proper formula.

The reductor shown in the accompanying sketch was used. This form of reductor was suggested by Mr. W. P. Barba of the Midvale Steel Co., a member of the sub-committee on Methods of the International Steel Standard Committee, and has been found most convenient.

In the bottom of the reductor tube A was placed a spiral of platinum wire, on top of this a piece of platinum gauze, a wad of glass wool six millimeters thick, and then a thin film of asbestos. The tube was filled with granulated zinc to within thirty-seven mm. of the top and a wad of glass wool twelve millimeters thick filling the diameter of the tube placed on top. This served to distribute the acid and to prevent the liberated hydrogen from spattering the solution on the upper part of the tube. The solution having been placed in the beaker B, the latter was placed on the stand C, and the tube D placed in position. The flask F having been attached, the block E was placed under it, and the pump having been connected the liquid was drawn over from B.<sup>1</sup> When the liquid in B was almost all

<sup>1</sup> See seq. for use of dilute sulphuric acid for washing.

drawn over, the sides of the beaker were washed down and then the beaker was filled with water, and when this was all drawn over, the stopper carrying the tube D was removed and the re-



ductor tube was filled with water to thoroughly wash out the top of the tube. The flask was removed, the end of the reductor tube washed into it, the sides of the neck of the flask washed down with water, and the reduced liquid was titrated in the flask.

In making a blank determination, the solution was made up as nearly as possible to the composition of the solution of the salt; *viz.*, twenty cc. ammonia, twenty-five cc. sulphuric acid (1-4) and water to the same volume.

In giving the results of our experiments, it seems unnecessary

to give all the figures as they comprise several hundred in number, extending over a period of six months. Only those illustrating the facts of interest are therefore annexed.

The most curious result obtained was in an effort to get the greatest possible reduction of the solution by repassing it through the reductor, heating it nearly to boiling after each passage. In the third passage, the solution instead of coming through green in color, was almost colorless and the green oxide of molybdenum was found deposited on the zinc in the reductor. In another attempt to reduce the molybdic acid by treating the solution in a flask with zinc in a current of hydrogen at a boiling temperature, redissolving the excess of zinc by sulphuric acid admitted through a funnel tube, allowing the solution to cool in the current of hydrogen after diluting by means of the funnel tube with boiled distilled water and titrating in the flask, the following results were obtained:

Weight of phosphomolybdate .....	0.08784 grams.
Volume of permanganate required .....	24.9 cc.-24.9 cc.
Molybdic acid on $\text{Mo}_2\text{O}_3$ theory.....	84.86 per cent.
“ “ “ $\text{Mo}_{24}\text{O}_{37}$ “ .....	87.28 “
“ “ “ $\text{Mo}_{12}\text{O}_{19}$ “ .....	89.85 “
“ “ “ Mo by grav. det .....	91.96 “

showing that the reduction was not even to  $\text{Mo}_{11}\text{O}_{16}$ .

A series of determinations was made to test the best rate of speed for passing the solution through the reductor, and for a column of zinc from two hundred to two hundred and fifty mm. no appreciable difference was noticed between a speed of two minutes and one of ten minutes for the passage of a solution made up in the usual way, except that it was necessary to follow the solution of phosphomolybdate by dilute sulphuric acid when the rate of speed was very slow to avoid leaving some molybdenum trioxide in the zinc. This precaution was finally made a part of every determination and the beaker which contained the solution to be reduced, was washed down with a hot solution of sulphuric acid (ten cc. of sulphuric acid (1-4) diluted to 100 cc.) and the operation was completed by washing with water. A speed of about two minutes was finally adopted with a hot solution. It was also found advisable to pour fifteen cc.

of sulphuric acid (1-4) into the titrating flask, before attaching it to the reductor.

The following results will illustrate the effect of dilution :

Weight of phosphomolybdate.	Volume of solutions in cc.	Potassium dichromate required in cc.	MoO <sub>3</sub> by Mo <sub>34</sub> O <sub>11</sub> theory. Per cent.
0.03095	175	9.0	88.83
0.03095	175	0.2	90.80
0.06190	175	18.35	90.55
0.06190	175	18.40	90.80
0.15475	175	46.40	91.59
0.15475	175	46.35	91.49
0.03589	500	10.1	85.76
0.14356	500	42.6	90.64
0.07178	500	20.9	88.94
0.14356	250	43.1	91.71
0.07178	250	21.0	89.36
0.14356	125	43.05	91.60
0.07178	125	21.5	91.49
0.09720	50	29.1	91.45
0.09720	50	29.05	91.29
0.09720	75	29.2	91.77
0.09720	75	29.1	91.45

These results all point to the fact that it is desirable to have the solution sufficiently concentrated, and a volume of 100 cc. was finally adopted as being most satisfactory for general use and for weights of phosphomolybdate up to two-tenths gram. With greater amounts of phosphomolybdate it is necessary to increase not only the volume of the solution but also the amount of sulphuric acid in order to prevent the reprecipitation of the ammonium phosphomolybdate in the acid solution.

Many variations in the manipulation were tried, such as passing a small volume of dilute sulphuric acid through the reductor, following this with the solution of phosphomolybdate without allowing any air to pass in and completing the operation by washing with dilute sulphuric acid and water which had been boiled to expel the air, but no higher results were obtained, and we concluded that the reduction was practically to Mo<sub>34</sub>O<sub>11</sub> and not to Mo<sub>3</sub>O<sub>4</sub>.

Secondly, to determine whether the methods in ordinary use would give results agreeing with these, it was determined to

send portions of this sample to the members of the sub-committee and also to Prof. Noyes and Mr. Doolittle. These samples were sent in the weighing tubes with the request that the tube be dried at  $100^{\circ}\text{C}$ . for about an hour and cooled in a desiccator. Then that about one gram be weighed out by difference, dissolved in ammonia, diluted to 250 cc. and portions of twenty-five cc. each measured off, acidulated and titrated in the usual manner; then that the results be returned in the following way; weight of phosphomolybdate used for the reduction, corrected volume of permanganate required for the oxidation, value of permanganate in iron. These returns were then calculated, giving the following interesting results.

$\text{MoO}_3$  IN SAMPLE 10 PHOSPHOMOLYBDATE.

	$\text{Mo}_2\text{O}_3$ theory. Per cent.	$\text{Mo}_3\text{O}_7$ theory. Per cent.	$\text{Mo}_{12}\text{O}_{39}$ theory. Per cent.	Gravimetric. Per cent.
Blair.....	88.91	91.45	94.14	91.96
Dudley .....	88.61	91.11	93.83	
Drown .....	88.68	91.21	93.90	
Shimer.....	88.22	90.74	93.41	
Doolittle (Job).....	90.47	93.05	95.80	
Noyes.....	89.95	92.52	95.25	
Average .....		91.68		91.96

May we not conclude from these results—

First, that the ratio of phosphorus to molybdic acid is 1.794?

Second, that the value of molybdic acid as compared with iron is 0.88163 according to the theory of reduction of the molybdic acid to  $\text{Mo}_3\text{O}_7$ ?

MOLYBDATE SOLUTION.

In the course of this investigation, our attention was naturally called to the stability of molybdate solutions and the composition of the yellow precipitate which forms sooner or later in nearly all these solutions.

This precipitate carefully collected, washed with dilute nitric acid and then with cold water and dried over sulphuric acid was bright orange colored and contained by analysis,

Molybdic acid.....	90.43
Water at $250^{\circ}\text{C}$ .....	9.61
Phosphoric acid .....	None
Ammonia .....	Traces

When heated the precipitate became white and was in fact molybdic anhydride. As ammonium phosphomolybdate is much less soluble in dilute nitric acid containing ammonium nitrate than in dilute nitric acid alone, we considered it possible that the excess of ammonium nitrate might be the cause of the instability of these solutions and an experiment showed this to be the case. We found that the solution prepared according to the following formula remained practically unaltered for several months and gave exactly the same results as a fresh solution when used for the determination of phosphorus in steel. The following is the formula and method of preparation:

One hundred grams of molybdic anhydride was thoroughly mixed with 400 cc. of cold distilled water and eighty cc. of ammonia (0.91 sp. gr.) was added. This completely dissolved the molybdic acid. The solution, after filtering to remove any silica or dirt, was poured into a mixture of 300 cc. nitric acid (1.42 sp. gr.) and 700 cc. water. The solution did not become very warm and there was very little tendency on the part of the molybdic acid to separate out during the mixing.

LABORATORY OF BOOTH, GARRETT & BLAIR,  
PHILADELPHIA.

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## THE FERRATES.<sup>1</sup>

BY CLAUDE A. O. ROSELL.

Received August 2, 1895.

“WHO has first seen ferric acid?” This question forms the pertinent title of a controversial article in the *J. Prakt. Chem.*, **32**, 448, and it is there stated that G. E. Stahl discovered that when saltpeter is ignited with iron and the mass is added to water, the caustic alkali resulting from the decomposition of the saltpeter holds a part of the iron in solution and produces an amethyst or purple color. He also stated that if dilute solutions of iron in nitric acid are poured in successive small portions into a strong solution of caustic potash the iron is dissolved on shaking, with a blood-red color.

While verifying the accuracy of the former I have not been able to reproduce the latter of these reactions. On its face it

<sup>1</sup> Read at the Brooklyn meeting.

looks so improbable that it must be believed that the statement is erroneous. Probably the nitric acid that Stahl used contained sufficient hydrochloric acid to make the reaction possible. Be this as it may, certain it is that the direction given by Stahl for making potassium ferrate in the dry way, through the ignition of saltpeter with iron, is sufficiently clear to be successfully followed, so that he is undoubtedly entitled to the credit of being the discoverer of ferric acid.

As recently as in Muir & Morley's edition of Watt's Dictionary of Chemistry, London, 1889, page 547, it is stated that "Stahl noticed in 1702 that a violet solution is obtained by fusing iron with saltpeter and washing with water or by adding a solution of iron in  $\text{HNO}_3$  to conc.  $\text{KOH}$  aq.," which shows that these two editors had nowhere found a correction of the erroneous statement of Stahl, nor has a correction been published by any one until now.

In 1802 potassium ferrate was rediscovered by Ekeberg, while fusing gadolinite, which is a silicate of yttrium, beryllium, and iron, with caustic potash. In this experiment the ferric oxide, of which the gadolinite contains sixteen per cent., was oxidized in the presence of caustic potash so as to form potassium ferrate. However, neither Stahl nor Ekeberg examined the character of the iron compound which resulted from the reaction with the caustic potash, either added or produced in the process, and which gave rise to the claret color observed.

When Fremy undertook an investigation of those compounds of the metallic oxides, in which the latter play the part of acid metallic anhydrides, he very soon rediscovered the solution of ferric oxide in caustic potash. In this solution he found that the oxide did not exist as ordinary ferric oxide,  $\text{Fe}_2\text{O}_3$ , but that it contained more oxygen than the latter, the quantity of oxygen contained corresponding roughly, or as closely as it was possible to analytically determine the constitution of an impure and somewhat variable body, such as barium ferrate, to the formula  $\text{FeO}_4$ , a result which has since been confirmed by J. Denham Smith and H. Rose.

The accounts of Fremy's work were published from time to time in a number of scientific periodicals, commencing with

January, 1841, when he states that the compound of oxide of iron and potash which is soluble in water corresponds in composition to the manganates, and in 1842 the new compound was called by him ferric acid, though the name had already been suggested by J. Denham Smith in *Phil. Mag. Ser. [3]*, 19, 302.

Besides producing potassium ferrate by the methods of Stahl and Ekeberg, which were unknown to him, Fremy also obtained it by electrolyzing caustic potash with an anode of cast iron and also by introducing chlorine into a solution of caustic potash containing ferric hydroxide in suspension. In addition he produced this salt by heating iron with potassium dioxide.

In attempting to produce sodium ferrate by such processes as Stahl and Ekeberg had used to produce potassium ferrate he failed. Not only did Fremy fail in his attempts to produce sodium ferrate in the dry way, but there is not to be found in the literature of the subject any account of anybody else who has succeeded in doing so or who has ever suggested the possibility of its being accomplished. In fact the statement occurs in chemical literature that sodium ferrate cannot be made except in the wet way. Thus in Wurtz' *Dictionnaire de Chimie*, Volume 1, Part 2, page 1413, the following is found: "Sodium ferrate is soluble in water and cannot be prepared except in the wet way."

Bloxam prepared a solution of sodium ferrate by adding bromine to a strong solution of caustic soda containing ferric hydroxide in suspension. This I have found a very quick and convenient method of producing a small quantity of a solution of sodium ferrate. I have also several times made the attempt to produce sodium ferrate by the addition of iodine to a solution of caustic soda holding ferric hydroxide in suspension, but no sodium ferrate was formed.

Bloxam also found that a solution of calcium ferrate may be produced by gently heating a solution of bleaching powder with a small portion of ferric chloride. On repeating this experiment I have found the process to be a very delicate one and that it often fails, although, if very carefully conducted a rose-red solution of calcium ferrate is formed. I thought that perhaps by the addition of lime to the bleaching powder solution the reac-



tion might take place more expeditiously. Such, however, was not the case, as a solution of calcium ferrate could never be produced when lime was first added to the bleaching-powder solution containing a small portion of ferric hydroxide in suspension.

It was first stated by Fremy and it has subsequently been repeated in the text-books that calcium ferrate, like barium ferrate, is insoluble in water. The experiment of Bloxam above referred to shows that this statement is not correct.

On preparing a solution of sodium or potassium ferrate allowing it to stand, it sometimes changes color from red to green. J. Denham Smith believed this green solution to be caused by some new iron compound, but Heinrich Rose showed that it was derived from manganese. The ferrate solution prepared contained a manganate. On standing, the ferrate decomposed while the manganate remained unchanged until at last only manganate remained, when the solution turned green. I have repeatedly verified the correctness of Rose's explanation.

In undertaking a course of investigation of the properties of ferric acid the following interesting problems presented themselves:

1. Production of sodium ferrate in the dry way.
2. Production of iron dioxide.
3. Decomposition of barium ferrate by metathesis so as to obtain in this way a normal ferrate containing no free alkaline hydroxide.
4. Determination of the constitution of the thioferrates.

#### I. PRODUCTION OF SODIUM FERRATE IN THE DRY WAY.

In the attempts to produce sodium ferrate in the dry way, ferric oxide, both dry and hydrated, was calcined with caustic soda, sodium carbonate, sodium nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate, but all in vain. The substitution of sodium chlorate for a part or all of the sodium nitrate was also tried but with no change in the result. Sodium dioxide was then tried, but at first without success. It was however observed that when the fused mass from this last experiment had been allowed to cool, on subsequent addition of water it became highly heated, and

it was suspected that while sodium ferrate had been produced by the reaction, that it was at the same time decomposed by the heat, resulting from the addition of the water, and it was believed that if this rise in temperature could be obviated the decomposition of the ferrate might be prevented. This theory was acted on and the mass resulting from the fusion of the ferric oxide and the sodium dioxide was treated with ice, and though some rise in temperature still followed it was much less than before, and sodium ferrate was obtained in solution. Thus the first problem had been successfully solved and sodium ferrate was for the first time produced in the dry way. There are two probable reasons why Fremy failed. In the first place, when using sodium nitrate this was to a great extent decomposed by the heat leaving behind sodium nitrite which is stable at high temperatures, and which, when the mass was dissolved in water served as a reducing agent, reducing the iron trioxide to the ordinary ferric oxide, while the nitrite itself, by oxidation, became converted into nitrate. When using caustic soda the cause of the failure was probably the heating of the mass on the addition of water, which heating has already been referred to.

## II. ATTEMPTED PRODUCTION OF IRON DIOXIDE.

The production of iron dioxide was of course the most important of the problems. The hope of accomplishing this result was the inciting cause of the investigation and a great number of experiments were conducted with this end in view.

As it is well known that chromium dioxide can be readily obtained by adding a solution of a chromic or chromous salt to a chromate it would seem at first sight that, having the iron monoxide and the trioxide, the iron dioxide might be easily prepared by an analogous reaction to the one above mentioned.

To produce a precipitate of iron dioxide from a solution of sodium ferrate, which is highly alkaline, the solution of the iron salt added would have to be alkaline. Such a solution may be made in many ways, such as by the addition of tartaric acid, citric acid, or glycerol, to a solution of a ferric salt and then adding a caustic alkali in excess, but in each case the organic solvent was oxidized before any precipitate was formed and so this method had to be abandoned.

The addition of barium ferrate to solutions of ferric chloride, both normal and basic, was tried with apparently good prospects of success as the barium went into solution as chloride, but at the same time oxygen and also chlorine were given off, so that the precipitate ultimately obtained consisted merely of ordinary ferric hydroxide. For the purpose of this experiment, the barium ferrate was just as good as normal sodium ferrate could this latter be produced; the barium ferrate decomposed the ferric chloride perfectly, so that if iron dioxide is capable of production, here the conditions of success seemed to be the best and yet the result of the reaction was only ordinary ferric oxide. Hence, it is quite certain that if iron dioxide can be made at all, it is a compound of such exceeding instability as to have decomposed as fast as formed.

### III. THE REACTIONS OF BARIUM FERRATE.

Of the ferrates the most stable, the one that can be prepared in the purest state and the most definite in composition is barium ferrate,  $\text{BaFeO}_4 \cdot \text{H}_2\text{O}$ , this formula having been determined by Fremy and H. Rose. Before barium ferrate has been allowed to dry it is decomposed by all the soluble acids, including carbonic acid. After it has once been allowed to dry in a desiccator it is not so easily decomposed, at least completely. If barium ferrate, which has not been allowed to dry, be suspended in water through which carbon dioxide is passed, it will be completely decomposed with the formation of barium carbonate and ferric hydroxide, oxygen being set free. From this decomposition it might reasonably be expected that iron dioxide would be formed just as manganese dioxide is formed on passing carbon dioxide through water containing barium manganate in suspension, but such is not the case. This experiment would also seem to indicate that neither a compound of iron, corresponding to a permanganate nor a compound corresponding to a bichromate exists. The result of passing carbon dioxide through water containing barium ferrate in suspension, with the object of obtaining new iron salts therefore carries with it two disappointments.

When barium ferrate has been thoroughly dried in a desicca-

tor it is readily attacked by acids, but complete decomposition is not readily effected in the cold even with dilute sulphuric acid, oxalic acid, formic or acetic acids. Hydrochloric acid decomposes it completely with the greatest readiness, chlorine being always set free. If barium chromate be digested with a solution of sodium ferrate, barium ferrate is formed and the solution changes color from red to yellow, due to the sodium chromate which has been formed. The reverse reaction never takes place. Thus, if barium ferrate is digested with a cold solution of an alkaline carbonate, sulphate or triphosphate, an alkaline ferrate is never formed, the solution remaining colorless. An alkaline sulphate will decompose barium ferrate that has not been dried with the formation of barium sulphate and ferric hydroxide, oxygen being set free. It thus appears that barium ferrate is one of the most insoluble salts known. It is strange that in none of the publications up to this time has the behavior of barium ferrate to neutral salts been referred to.

#### IV. THIOFERRATES.

Freymy states that on passing hydrogen sulphide through a solution of sodium ferrate a solution is obtained of a beautiful emerald color. He supposed that the sodium ferrate was converted into sodium thioferrate. On passing hydrogen sulphide through a solution of sodium ferrate I sometimes obtained the green solution described by Freymy and at other times not. Investigating the matter, I found that the green solution was obtained only when the original solution contained manganese. It appears then that on passing hydrogen sulphide through a ferrate solution containing a manganate the ferrate is reduced by the hydrogen sulphide, leaving the green manganate solution behind. If, on the other hand, the ferrate solution contains no manganese, on passing hydrogen sulphide through it, the red color disappears and a solution is obtained having a greenish yellow tinge, such as is obtained by digesting precipitated iron sulphide in a solution of an alkaline polysulphide, the greater part of the iron being precipitated as black sulphide. The supposed thioferrates must therefore be considered as mythical.

The only use so far suggested for the ferrates, is the produc-

tion of oxygen described in British Patent, No. 85, Jan. 10, 1886, to Brooman, a communication by Maréchal and Tessie duMotay, in which it is stated that potassium, sodium, and barium ferrate may be decomposed by a current of steam and subsequently reformed by the action of a current of air at high temperature.

Whether the ferrates resemble the chromates or manganates more is difficult to say. If a salt could be produced corresponding, either to the bichromates or the permanganates the question would of course be immediately decided. The extreme insolubility of barium ferrate, together with the solubility of calcium ferrate, as well as the instability of the dioxide, if it does exist, brings the ferrates closer to the chromates than the manganates. On the other hand the soluble ferrates can only exist in alkaline solutions, and in this respect they resemble the manganates. In their oxidizing power the ferrates still more closely resemble the manganates. It has already been stated that a ferrate will oxidize nitrites, tartrates and glycerol. The soluble ferrates are also decolorized or reduced by oxalates, alcohol, ether, ammonia, urea, and other soluble organic bodies with very few exceptions, such as, and notably, the acetates. They are decomposed also by some insoluble organic bodies, such as paper and insoluble carbohydrates, but most insoluble organic bodies, such as the paraffines and benzene, decompose them but very slowly.

To perform all the experiments on ferrates above referred to, sodium and potassium ferrate had often to be prepared. Of all the methods of making these salts the easiest is to pass chlorine through a strong solution of sodium hydroxide, containing ferric hydroxide in suspension. At one time I produced sodium ferrate on a scale never before attempted. Three kilos of sodium hydrate were dissolved in enough water to form ten liters of solution. To the solution were added 150 grams of ferric chloride, and the mixture stirred for a long time until the ferric hydroxide formed was all finely divided and evenly distributed throughout the solution. Through the mixture chlorine gas was then passed from a cylinder of liquid chlorine which had kindly been presented by my friend Dr. Rudolph Knietsch, one of the leading chemists of the Badische Anilin und Soda Fabrik of Ludwigs-

hafen, Germany. The operation was carried on very successfully, the chlorine gas passing through with great regularity, and in this manner a quantity of stock solution was prepared sufficient for all subsequent experiments.

It may here be stated that whenever an experiment is described above it has been actually tried for the purpose of making sure that the reaction indicated actually takes place.

The following is a summary of the errors which occur in the literature of ferric acid:

1. The direction for making potassium ferrate by adding iron nitrates to caustic potash, by Stahl.
2. The statement that on standing a solution of potassium ferrate changes color and turns green, made by J. Denham Smith.
3. The statement that calcium ferrate is insoluble in water, made by Fremy.
4. The direction for making thioferrates by passing hydrogen sulphide through a solution of a ferrate, by Fremy.
5. The allegation that sodium ferrate cannot be made except in the wet way, made by Wurtz.

Of these, the second error was corrected by H. Rose and the third by Bloxam, the other three having now for the first time been brought to light.

In the annexed bibliography are included only original articles, and when articles have been reprinted in different periodicals, only the first has been given. The full titles of the articles referred to have been perused, so that it is certain that they exist and relate to the subject-matter indicated.

#### BIBLIOGRAPHY.

1844. G. E. Stahl, 1702, referred to in *Journal für Praktische Chemie*, 32, 448, but a copy of Stahl's writings has not been attainable.

1802. Ekeberg, *Könliga Vetenskapsakademiens Handlingar*, p. 68. Upplysning om Ytterjordens egenskaper i synnerhet i jemförelse med Berylljorden; om de Fossilier, hvori förstnämnde jord innehalles, samt om en ny upptäckt kropp af metallisk natur af A. G. Ekeberg. (Description of the properties of yttrium oxide, especially in comparison with beryllium oxide, of the fossils, in which the former oxide is contained and of a newly discovered body of metallic nature by A. G. Ekeberg.)

1832. Bequerel, *Ann. Chim. Phys.*, [2] 51, 105: De la cristallisation de quelques oxides métalliques.

1841. Fremy, *Compt. Rend.*, 12, 23: Recherches sur l'action des peroxides alcalins sur les oxides metalliques.
1841. Poggendorff, *Ann. der Phys. Pogg.* 54, 371: Bildung der Eisensäure auf galvanischen Wege.
1841. J. Denham Smith, *Phil. Mag.*, [3] 19, 302: Experiments on the alleged conversion of carbon into silicon.
1842. Fremy, *Comp. Rend.*, 14, 442: Recherches sur les acides metalliques.
1843. H. Rose, *Ann. der Phys. Pogg.* 59, 315: Über die Zusammensetzung der Eisensäure.
1843. J. Denham Smith, *Phil. Mag.* [3] 23, 217: On the Composition of an Acid Oxide of Iron (ferric acid).
1844. Fremy, *Ann. de Chemie*, [2] 12, 365: Recherches sur les acides metalliques.
1844. *Ann. der Phys. Pogg.* 62, 288: Wer hat die Eisensäure zuerst gesehen?
1844. *Prakt. Chem.*, 32, 448: Wer hat die Eisensäure zuerst gesehen?
1879. W. Foster, *Ber. d. chem. Ges.* 12, 846: Notiz über die höhern Oxyde von Eisen, Chrom, Mangan, und Wismuth.
1886. Bloxam, *Chem. News*, 54, 43: Lecture Experiment. The Ferrates.

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA SUGAR  
EXPERIMENT STATION AND SUGAR SCHOOL.]

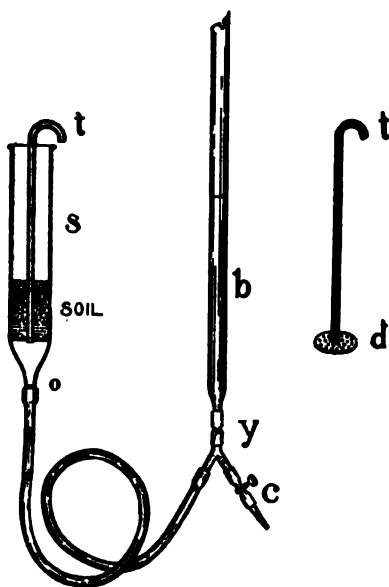
### A SIMPLE AND CONVENIENT APPARATUS FOR ESTIMATING THE WATER-HOLDING POWER OF SOILS.

BY J. L. BEESON.

Received June 3, 1895.

TO a fifty or 100 cc. plain burette is connected a glass Y tube by means of a piece of rubber tubing. To one of the forks is attached a bit of rubber tubing carrying a pinch-cock, and the other fork is connected with a small Stutzer extraction tube, having a zero mark scratched on its neck, by means of a stout piece of rubber tubing about two and one-half feet long. The apparatus is fastened in the clamp of an ordinary clamp-stand. A metallic disk, which will about fit the larger tube, is perforated with many small holes, the center with a larger hole that will admit the end of a piece of glass tubing, which is made firm by

fusing into the glass by means of a burner or blast lamp. The upper end of the tube, d t, is bent over so that the soil will not fall into it while filling the larger tube. Disks of filter-paper, of convenient size, are perforated with a cork borer, and one of



these is slipped over the glass tube down against the perforated disk, and held down by means of a rubber washer cut from a piece of small rubber tubing. The edges of the paper are folded under the tube well, and the whole slipped down to the bottom of the large tube. The apparatus, which is now ready for use, is very simple, and much more rapid and convenient, it is believed, than the one devised by Mr. Feulling as described in Dr. Wiley's book on soil analysis. The apparatus is filled with water, the

burette raised so as to cover the disk and filter-paper and then lowered. The excess of water will now run out of the filter-paper so that the reading will become constant within five minutes. Then by means of the pinch-cock c water is slowly drawn off until it stands at the zero mark on the neck of the tube o, and at zero on the burette. From twenty-five to fifty grams of soil, according to the water-holding power of the sample, is added to the large tube S, which is gently tapped until the soil is level. The burette is raised and the water gently forced into the soil from below until it forms a level above the soil. From the height of the column of water in the air-tube t the amount of pressure may be seen. The burette is then lowered and the water runs out of the soil by gravity alone, since the space below the disk is supplied with air through the tube t. When there is no more rise of water in the tube, which requires about fifteen to



twenty minutes, the burette is raised until the water stands at the zero mark *o* in the tube, when the number of cc. of water absorbed by the soil is read on the burette. The whole time for an analysis need not exceed thirty or forty minutes. The pinch-cock on the Y tube is most convenient in bringing the water to the zero marks on the tube and burette before adding the soil. The apparatus may be obtained of Kähler and Martini, Berlin.

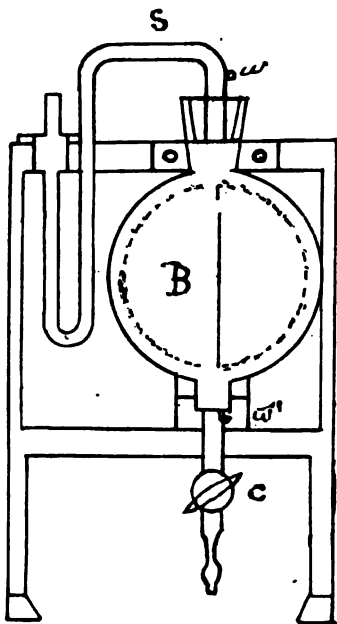
### A MODIFICATION OF HINMAN'S EXPLOSION PIPETTE.

By AUGUSTUS H. GILL.

Received August 7, 1895.

THIS pipette was devised to permit the use of all the residue, sixty cc., remaining after an illuminating gas had been analyzed by the Hempel apparatus, in mixing with oxygen for explosion.

It consists of a bulb, *B*, eleven to twelve cm. in diameter, of about 250 cc. capacity, with walls at least twelve mm. thick, provided with two tubulatures; at the bottom a stop-cock, *C*, is ground in for regulating the flow of mercury; to the top one is fitted the capillary stem, *S*, which must be very carefully ground in. These joints are first vaselined, care being taken that none gets inside the apparatus, and cemented in with a sealing wax having nearly the same coefficient of expansion as glass. Metal clamps hold the bulb upon the stand, similar to that for the simple pipette,<sup>1</sup> the weight of the bulb being sufficient to keep it in the lower one; the upper one is provided with screws to hold the neck of the bulb. To render the stem-joint more nearly tight the upper tubulure is made with a mercury seal an inch deep. As thus constructed, the apparatus is



<sup>1</sup> Gill, *Am. Chem. J.*, 14, 231.

absolutely tight at all pressures to which it is likely to be subjected.

Both spark wires were originally fused through the capillary stem, but from the oxides of nitrogen and carbon dioxide formed during the explosions an electrical connection was established sometimes between them and no spark was visible upon turning on the current. To obviate this, one fine spark wire,  $w$ , is fused through the capillary and the other,  $w'$ , a platinum wire one and a half mm. in diameter passes through a rubber fitting in the tube carrying the stop-cock up through the mercury to within two mm. of the other. A Mariotte bottle conveniently serves as a reservoir for the mercury and is connected with the pipette by quarter inch "pressure tubing."

It sometimes happens that no spark passes upon closing the circuit. This can be remedied by sucking water into the pipette and expelling it. Upon allowing it to stand all the moisture rises to the top and may be driven out.

The apparatus has been in use for four years, scores of explosions having been made with it. It may be obtained from the Ziegeler Electric Co., Franklin St., Boston.

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### ESTIMATION OF SULPHUR IN PYRITES.

BY G. LUNGE.

Received June 4, 1895.

IN this Journal Mr. Gladding replies to my remarks on his previous paper on the estimation of sulphur in pyrites. His comments would certainly not give to any reader, who had not my own paper before his eyes, a fair idea of its purport. He states that I admit "that every modification proposed (by Gladding) is accurate in its nature, with one single exception." This conveniently passes over the fact that my "admission" had been saddled with the following addition, for which I had adduced ample experimental proof, "that not in a single case is Gladding's method more correct than mine, and that his modifications cannot be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever."

In one point, and that just relating to the principal novelty in Gladding's process, I declared him to be entirely *wrong*; viz., in his denial of the fact that it is very easy, by a special kind of washing, to avoid leaving any sulphur in the ferric hydroxide. This point is even more decidedly misrepresented by Gladding (of course, unintentionally) than the others. He says that I "admit that students in my own laboratory have sometimes failed to get out all the sulphur, through imperfect washing." I must really complain of this way of quoting my paper against myself, seeing that I immediately followed up the above by the express statement that such failures occurred in *every* case through having washed in the usual way, instead of the special way prescribed by me for that object; and that the same men have succeeded in every case after their attention had been drawn to this point. That beginners, like those I was speaking of, will make mistakes in most other analytical methods as well, until their attention is drawn to their having neglected some essential precautions, is too patent to be dwelled upon. Nor is it my business to find out why Mr. Gladding and his assistants have failed in a process which succeeds in the hands of *all* beginners in my laboratory, and which is practised by hundreds of chemists, none of whom have ever found any fault with it.

After such an involuntary "admission" of imperfect manipulation on Mr. Gladding's part, it is not possible to take the accuracy of his further results for granted which are contradictory to mine, concerning the differences between our two methods. I repeat that I have afforded in my paper, by a large number of comparative assays, complete proof that (except when the washing was intentionally interrupted before completion) absolutely the same results are obtained by both methods, mine, however, taking considerably less time than his. It seems to me perfectly unnecessary to repeat such proofs, since nothing new can possibly be brought out by it, and I must altogether decline to carry on further discussion with an opponent who treats my paper and work in the above-mentioned style, rewarding my studied fairness by construing it into all sorts of distorted "admissions," and not appreciating the perhaps exaggerated courtesy with which I had explained a decided error in his description of the

decomposing-mixture as being perhaps due to a clerical mistake.

Mr. Gladding seems to have felt that it was necessary to bring heavier metal against me than his own assertions, and he therefore quotes a private communication from Prof. Richards, of Harvard College. He does not mention anything of Prof. Richards having sanctioned the verbatim publication of the "private" communication. For my part, until the contrary is proved, I beg leave to doubt that Prof. Richards would *publicly* have used expressions accusing me of ignorance on a point "which has been known for a number of decades;" *viz.*, the occlusion of barium chloride on the sulphate. Before doing so, he would have looked not merely at my last paper, but also on those I had previously written on the estimation of sulphur in pyrites. He would then have found that I have made researches on this subject for the last fifteen years, and that in my communications the previous work of Fresenius, concerning the difficulty of removing the barium chloride from the sulphate, is referred to as common knowledge. He would then not have misunderstood my last paper as denying that patent fact, which he has so thoroughly investigated in a paper published subsequently to mine. He would have acknowledged that I could not have meant anything else than claiming for my special process the greatest possible approach to truth, which would *not* be attained by preventing all and every occlusion of barium chloride, seeing that the solubility of the barium sulphate in the acid liquid must cause an error in the opposite direction. I am quite sure that Prof. Richards, like every other chemist, is aware of the fact that not one of our analytical separations is mathematically perfect, and that the best analytical methods are those in which unavoidable, but opposite errors are as nearly as possible balanced, and which thus gives a closer approximation to the truth than methods in which one of these errors is eliminated, but the compensating error in the opposite direction is allowed to remain. I have never claimed that the precipitate of barium sulphate obtained according to my method was absolutely devoid of barium chloride, no more than, in the opposite direction, that no barium sulphate whatever remained dissolved in the acid liquor; my claim has been that my method, by compensation of unavoidable errors, gives *correct*

results. I need not, however, comment any further upon Prof. Richard's private letter to Mr. Gladding, since everything of importance in this controversy is settled by an authority which Prof. Richards will certainly approve of; viz., a passage in his own paper in the *Zeitschrift für anorganische Chemie*, 1895, 8, 418, which I translate verbatim:

"Moreover the observation is of interest, that the error caused by occlusion ordinarily just about compensates that caused by the solubility of the sulphate, so that the final corrected result is almost the same as the real weight. The average of the uncorrected results is 0.3215 in lieu of 0.3214 gram."

This, I think, disposes of the aid which Mr. Gladding has solicited from Prof. Richards in his attack upon me.

ZURICH, MAY 23, 1895.

### THE PERIODIDES.<sup>1</sup>

BY ALBERT B. PRESCOTT.

Received August 12, 1895.

THE periodides are remarkable as products of extreme additive combination, along with clearly cut crystalline form, distinct physical constants, and instances of rare optical power. They are easily reduced to normal iodides, containing for every atom of iodine firmly bound, one or more iodine atoms loosely bound; therefore they are often and not improperly termed superiodides. Professor Geuther used for them the term polyiodide, perhaps by reason of his view that all their iodine atoms are of equal valence in the molecule.<sup>2</sup> Jörgenson designated them together as superiodides, though including within their structural type certain double polyiodides not understood to contain additive iodine.<sup>3</sup> If these compounds contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked. The one iodine atom that is directly united to the nitrogen or other

<sup>1</sup> Read at the meeting of the American Association for the Advancement of Science, Springfield, Aug. 30, 1895.

<sup>2</sup> A. Geuther, 1887: *Ann. Chem. (Liebig)*, 240, 82.

<sup>3</sup> M. Jörgenson, 1869: *Ber. d. chem. Ges.*, 2, 465.

base-forming element, by virtue of this union, enables a number of other iodine atoms (say from two to eight) to unite with each other together with itself in an iodine group, capable of forming multiples in polybasal molecules. To this view we are led, possibly misled, by the course of theory. In this relation the molecular weight of free iodine is of interest, and has been studied with care, not only in the vapor<sup>1</sup> but in solutions<sup>2</sup> and in the crystals<sup>3</sup> themselves. The relation to the elemental molecules gives to the periodides an interest greater than that of the mixed superhalides, such as iodoperchlorides and iodoperbromides of bases inorganic and organic. The supersulphides, however, present a corresponding instance of additive combination with a single element, as understood. The organic supersulphides<sup>4</sup> are not so ready of formation or so stable as the organic superiodides, though the reverse seems to be true of the corresponding inorganic super compounds. In its elemental states sulphur surpasses iodine in its unusual capacity for polyatomic molecules. And this comparison holds for the hydrides, as hydrogen pentasulphide was reported in 1888<sup>5</sup>, while hydrogen diiodide, though holding a name in the earlier handbooks<sup>6</sup> is no longer accounted a chemical individual.<sup>7</sup> Again, the superoxides of organic acid radicals were compared with superiodides by Brodie.<sup>8</sup>

To obtain a general survey of the principal known periodides, they may be provisionally classified, chiefly with respect to their bases, as follows :

1. The periodides of potassium and of mercury. Any double metallic polyiodides containing additive iodine and without other acid.

<sup>1</sup> V. Meyer, 1880: *Ber. d. chem. Ges.*, 13, 1010; Neumann, 1880: *Ber. d. chem. Ges.*, 13, 1050.

<sup>2</sup> M. Loeb, 1888: *J. Chem. Soc.*, 53, 805; Paterno and Nasini, 1888: *Ber. d. chem. Ges.*, 21, 2153; Krüss and Thiele, 1894: *Ztschr. anorgan. Chem.*, 7, 52; John Couroy, 1874: *Proc. Roy. Soc.*, 25, 46.

<sup>3</sup> John Couroy, 1876: *Proc. Roy. Soc.*, 25, 51; Compare Geuther, 1887, *Ann. Chem. (Liebig)*, 240, 85.

<sup>4</sup> Palm, 1863: *Phar. Ztschr. Russ.*, 2, 337, 361, 385; A. W. Hofmann, 1868: *Ber. d. chem. Ges.*, 1, 81; E. Schmidt, 1876: *Ann. Chem. (Liebig)*, 180, 287; A. W. Hofmann, again in 1877, *Ber. d. chem. Ges.*, 10, 1087.

<sup>5</sup> Rebs: *Ann. Chem. (Liebig)*, 246, 356.

<sup>6</sup> Gmelin's Handbook, 2, 261, 1849, from Baup, *J. Pharm.*, 9, 40.

<sup>7</sup> Gmelin-Kraut's Handbuch, I, 2, 310, 1872.

<sup>8</sup> *J. Chem. Soc.*, 2, 281, 1876.

2. Periodides of ammonium. Periodides of arsonium<sup>1</sup> and of stibonium if they have been obtained. Periodides of the metallic derivatives of ammonium. The same of metallic derivatives of arsonium and of stibonium, if they have been obtained.

3. The periodides of organic bases. They are mostly of the quaternary, and the tertiary<sup>2</sup> bases, of the nitrogen-base family, including bases with oxygen and without it. Phosphonium,<sup>3</sup> arsonium,<sup>4</sup> and probably stibonium<sup>5</sup> periodides are known. And, of another type, that of perhalide of a bare amine base, such as  $(R_3N)I_2 \cdot I$ , at least triethyl phosphine periodide<sup>6</sup> and pyridine periodide<sup>7</sup> have been reported. Also a perhalide taken as pyridine dibromide hydrobromide.<sup>8</sup> The nitrogen-base periodides belong in two categories, (1) those of the alkylammonium bases, and (2) those of pyridine and its derivatives. Polyiodides of the vegetable alkaloids belong in the latter division, except the caffeine and theobromine polyiodides.

4. The periodide of iodonium, the organic iodine base obtained by Victor Meyer last year.<sup>9</sup> The normal iodide of iodonium is of structural interest to polyiodides generally.

5. Aromatic sulphon periodides, as found by Kastle and Hill last year.<sup>10</sup>

6. Acid polyiodides, more or less complex, and double base polyiodides, inorganic and organic, including those in which the iodine is not in additive combination, that is, *not* yielding a distinct part of the iodine to reducing agents with a good end reaction.

<sup>1</sup> Phosphonium normal iodide; Labillardière and Gay Lussac: *Ann. chim. phys.* [2], 6, 394; A. W. Hofmann, 1887; *Ann. Chem.* (Liebig), 103, 355; 1873: *Ber. d. chem. Ges.*, 6, 286. Inflames by contact with iodine.

<sup>2</sup> In Geuther's table, in 1887, of the periodides then known, the only periodides of tertiary bases destitute of oxygen, which appear are a pyridine hydrogen pentiodide, and a quinoline hydrogen tetriodide, both by Dafert (Geuther: *Ann. Chem.* (Liebig), 240, 74). In reporting upon these, in 1883, Dafert says: "Nach den bis jetzt bekannten Thatsachen schientes, dass nur tertiäre und Ammoniumbasen Periodide bilden" (*Monatsh. Chem.*, 4, 510.)

<sup>3</sup> Tetraethylphosphonium triiodide, Jörgensen, *Ann. Chem.* (Liebig), 240, 74.

<sup>4</sup> Tetraalkylarsonium triiodides, Cahours, 1860: *Ann. Chem.* (Liebig), 116, 346; 1862: *Ibid.*, 122, 215.

<sup>5</sup> Jörgenson, 1869: *Ber. d. chem. Ges.*, 2, 463.

<sup>6</sup> Masson and Kirkland, 1889: *J. Chem. Soc.*, 55, 139.

<sup>7</sup> Mr. Trowbridge and the author in another paper of this date.

<sup>8</sup> Grimaux, 1882: *Compt. rend.*, 95, 87; *Bull. Soc. Chim.*, 38, 127.

<sup>9</sup> *Ber. d. chem. Ges.*, 27, 1594, 1894.

<sup>10</sup> *Am. Chem. J.*, 16, 116. A sulphur periodide of another order is that obtained in amorphous condition by Jörgensen, 1869: *Ber. d. chem. Ges.*, 2, 464.

Geuther's classification into triiodides, pentaiodides, hepta-iodides, and enneaiodides, all with one atom of iodine firmly bound,<sup>1</sup> was of service in his own study of structural features. But Geuther admitted a category of sesqui-, di-, tetra-, and hexa-iodides. There is surely a prevailing proportion of *even* numbers of *additive* iodine atoms, making *odd* numbers of *total* atoms of iodine, per "molecule" of the periodide. Generally this is an assumed "molecule" of monobasal proportions. That two or more monovalent groups of the ammonium type should enter into the formation of a periodide molecule, in some cases, is theoretically probable, to say the least, if periodides are individualized in molecules at all. The hypothesis of Jörgenson in 1869,<sup>2</sup> providing for both monammonium and diammonium types of periodides, is not an unreasonable one. Moreover, there is to be considered the probable occurrence of an iodine atom in the fourth position of the organic ammonium group, phosphonium group, etc., with whatever degree of firmness of binding may be determined for it in this position. Take it all in all, therefore, it seems to me that at present we know no law of even or uneven numbers of iodine atoms in superiodides, either to help or to hinder our interpretation of results. With evidence of molecular weight we may gain approach to such a law.

In division 6 of the classification above there are without doubt included certain strictly normal iodides. The iodomercurates as strongly marked double iodides, and the Herapathites as representative acid superiodides come in this division. An interest in the iodomercurates of the nitrogenous bases<sup>3</sup> has been but one among several causes contributing to my own interest in this subject at present. But I have not yet made such an inquiry into the action of deiodinizing agents upon the known double iodides as might reveal what superiodides there are among them. Some of the tabulations of the super-iodine in double inorganic polyiodides given by Geuther<sup>4</sup> seem to invite further inquiry. The acid periodides in many cases undenia-

<sup>1</sup> *Ann. Chem.* (Liebig), 240, 74, 80, 1894.

<sup>2</sup> *Ber. d. chem. Ges.*, 2, 465, 1869.

<sup>3</sup> *Am. Chem. J.*, 14, 607, 1892; 2, 294, 1880. *Pharm. Rund.*, 12, 146.

<sup>4</sup> *Ann. Chem.* (Liebig), 240, 81.



bly contain additive iodine, but the question of their constitution, like that of mixed halides in general<sup>1</sup> is more complicated and is perhaps of less special significance, than that of the simple polyiodides.

With the exception, then, of the metallic, the iodonium and the sulphon periodides, the formation of superiodides is limited, so far as I have found, to compounds of the nitrogen family of elements.

The first periodide recognized, so far as I find record, may have been that of ammonium, termed by Berzelius the biniodide. After the discovery of iodine the first workers upon the alkaloids seem to have mistaken, in some instances, a produced periodide for a mixed excess of iodine to be taken up by more alkaloid in preparation of the hydriodides.<sup>2</sup> In 1839 Bouchardat,<sup>3</sup> a medical writer in Paris, recounts that, when dogs were being surreptitiously poisoned with strychnine in Paris, and an antidote was asked for, first Guibourt recommended powdered galls, and then Donné advised iodine tincture,<sup>4</sup> whereupon Bouchardat himself, approving the use of iodine, said they should use it in potassium iodide solution. He then set forth some interesting characters of the alkaloid periodides, comparing them with ammonium periodide, quoting for this the name from Berzelius mentioned above. De Vrij has said that Bouchardat anticipated Herapath in production of iodosulphates. A modest memoir of Donné, in connection with the Parisian interest just referred to, upon the use of iodine as an analytical reagent for vegetable bases, was referred for criticism to D'Arcet and Chevreul, who made quite an elaborate report<sup>5</sup> upon the action of free chlorine, bromine, and iodine, in intensive application, with admonition as to undue dependence upon any single analytical reactions. In 1846, in his summary of the distinguishing reactions of the more important

<sup>1</sup> The Chloriodides of Organic Bases, and Pyridine Chloriodide, Pictet and Krafft, 1892: *Bull. Soc. Chim.* [3], 7, 72.

<sup>2</sup> Pelletier and Caventou, 1819. *Ann. chim. phys.* [2] 10, 142; *Ann. der Phys.* *Albert*, 63, 306.

<sup>3</sup> Bouchardat, 1839: *Compt. rend.* 9, 475; *L'Institut*, 7, 358.

<sup>4</sup> Both apparently acting under the opinion, due to that little chemistry which has often brought all chemistry into disrepute, that a precipitant in a test-glass will serve as an antidote in the stomach.

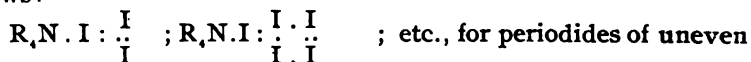
<sup>5</sup> *Ann. chim. phys.* [2] 38, 82.

alkaloids,<sup>1</sup> v. Planta-Richenau specifies for each a precipitation by free iodine. In 1854, shortly after A. W. Hofmann's famous elucidation of organic ammonium bases,<sup>2</sup> Weltzien contributed a full and careful description<sup>3</sup> of the tetramethyl and tetraethyl ammonium triiodides. In 1858 Müller added a good account<sup>4</sup> of quaternary mixed alkyl ammonium triiodides. In 1866 Wagner<sup>5</sup> proposed iodine precipitation and a method of treatment of the periodide precipitates for separation of alkaloids from extractive matters. And Tilden made a contribution in 1866.<sup>6</sup>

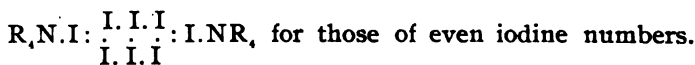
The masterly work of Jörgensen, beginning with his dissertation at Copenhagen in 1869, continuing for about nine years<sup>7</sup> in this field, and extending over nearly all relations of polyiodides in general, have had the respect of all chemists, while hardly yet fully assimilated.

In 1887 this subject was taken up by Professor A. Geuther, at Jena, who contributed<sup>8</sup> a good number of new periodides from his own laboratory, with a tabulation of all then obtained, and a vigorous and independent study of the features of structure. The crystallographic investigations were made by Prof. Lüdecke. Prof. Geuther died in 1889.

In 1869 Jörgensen<sup>9</sup> formulated his idea of the probable structure of "these compounds," taking iodine as trivalent, as follows:<sup>10</sup>



numbers of iodine atoms.



And  $R_4N \cdot I : \begin{array}{c} I \\ I \end{array} : Hg$  for a typical iodomercurate. This simple

<sup>1</sup> Heidelberg dissertation, 1846. *Ann. Chem. Pharm.*, 74, 245.

<sup>2</sup> 1850-51: *Phil. Trans. I.* 93-131, 357-398.

<sup>3</sup> *Ann. Chem. Pharm.*, 91, 33; 99, 1.

<sup>4</sup> *Ann. Chem. Pharm.*, 108, 1.

<sup>5</sup> *Ztschr. anal. Chem.*, 4, 387.

<sup>6</sup> *J. Chem. Soc.*, 19, 145, 1871.

<sup>7</sup> *J. prakt. Chem.*, 1870-78, [2] 2, 347, 433; 3, 145, 328; 14, 213, 356; 15, 65, 418; 16, 352. *Ber. d. chem. Ges.*, 2, 460, 1869.

<sup>8</sup> *Ann. Chem.* (Liebig), 240, 66-91.

<sup>9</sup> *Ber. d. chem. Ges.*, 2, 465, 1869.

<sup>10</sup> The present writer gives  $R_4N$  as an expression for any organic base of nitrogen, instead of "Alk" used by Jörgensen.

conception is, of course, consistent with an iodine valence of five or of seven.

Geuther<sup>1</sup> drew from the optical studies of the color of iodine crystals by Conroy the indication that the molecular mass of the crystalline element is that of  $(I_8)_n$ . He made this generalization as to color of the periodides, that the tri and hepta iodides were red-brown to violet-blue, and the penta- and enneaiodides green to green-black, the higher iodine numbers giving the deeper shades.<sup>2</sup> He presents structural schemes of orders as follows:

For the triiodides,  $(R_3I_3)I_{12} = 6(RI_3I_3)$ ; for the heptaiodides,  $(R_7I_7)I_{12} = 2(RI_7I_7)$ ; for the pentaiodides,  $(R_5I_5)I_{12} = 4(RI_5I_5)$ ; and for the enneaiodides,  $(R_9I_9)I_{12} = 2(RI_9I_9)$ .

In the laboratory of the writer the preparation of periodides of pyridine is in the hands of Mr. P. F. Trowbridge, and an account of some of these is communicated by both of us in another paper, while he continues the work for pyridine and quinoline. Some work on periodides of the more simple of the aliphatic bases is in other hands. In this subject a pyridine normal polybromide, namely a trimethylene bromide, obtained by Mr. R. F. Flinterman, is reported upon in a paper by him and myself. Therewith it is desired to continue studies of the limit of tertiary base addition to halogen alkyls which are secondary and tertiary. I submit also a note with the observations of several workers upon the preparation and properties of a few pyridine alkyl normal iodides, and Mr. S. H. Baer has some work in progress with me upon pyridine alkyl hydroxides.

ANN ARBOR, MICHIGAN.

## AN IMPROVED GAS REGULATOR.

BY F. P. DUNNINGTON.

Received August 7, 1895.

SOME years ago I published<sup>1</sup> a description of a gas-regulator, which is now so modified as to make it less bulky and more reliable. Its arrangement may be understood by reference to the

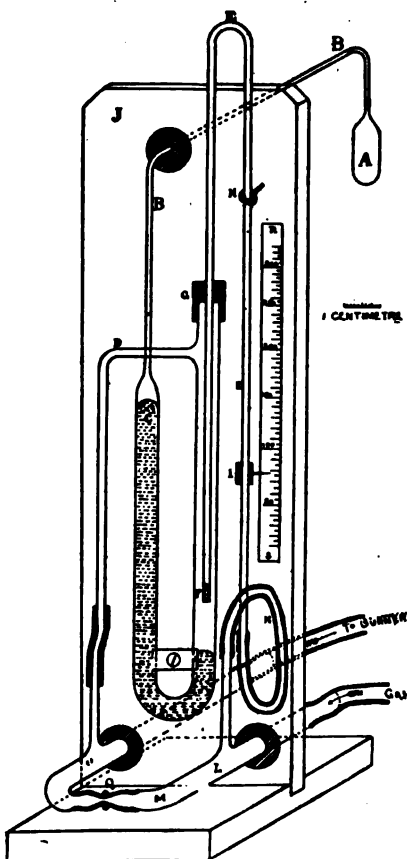
<sup>1</sup> *Ann. Chem. (Liebig)*, 240, 85.

<sup>2</sup> This generalization, to which Prof. Geuther acknowledged reported exceptions, finds little support in the observations which Mr. Trowbridge and the writer have been able to make.

<sup>3</sup> *Am. Chem. J.*, 4, 2.

figure, with the accompanying scale the measure of the inner walls of the tubes may be ascertained, and other dimensions are drawn to two-thirds of this scale.

The tube B with stout walls, about forty cm. long is attached to the bulb A. Into the tube C, thirty-five cm. the small side tube D is fused. Unite C to B, and bend all as indicated. Into the tube L, fuse the side tube and at M, bend at right-angles; similarly make the tube O. These latter are passed through corks, set in the upright board J. B also is passed through this board, which then serves to screen the apparatus from the heat of the bath, and C is firmly fastened to it.



The light tube E, fifty cm. long terminates at F with a slit, made by blowing a hole through its side and then drawing it out. This slides through a joint at G, made with two sections of rubber tubing, and also through a screw-eye at H. Upon E slides a bit of rubber tubing I, which is compressed by a wire around it, the end of which serves as an index. E is connected to L, by

fifteen cm. of light one-eighth rubber tubing, D is connected with O, and L is joined to O by a rubber tube pinched by a screw clamp at Q. A piece of card-board, RS, is pasted to the board. By warming and cooling the tube C is filled with mercury, as indicated. To graduate the apparatus, connect L with gas supply and O with a burner, pinch the tube at N, open Q sufficient

to maintain a small flame, relieve N and push down E until the flow of gas through F just ceases; then slide the index I almost to the lower end of E, and upon the paper mark the point corresponding to the temperature of the bulb A. Place bulb A and a thermometer in a water-bath, with the burner beneath, and raise E. When the temperature of the bulb A is, say  $50^{\circ}\text{C}$ , lower E until the flow of gas through F just ceases, and make a mark on the scale for  $50^{\circ}$ , similarly fill out this scale to  $100^{\circ}\text{C}$ ., and for higher temperatures employ an air-bath, or preferably a paraffin bath.

In using the apparatus, E is lowered until the gas through F is just cut off and the index is moved up or down the tube until it points to the figure marking the temperature of the atmosphere in which A is exposed. Having fixed the index, the tube E is raised until the index marks the temperature at which it is desired to maintain the bulb.

This adjustment of the index, whenever the regulator is used, eliminates the effect of the thermometer and barometric pressure upon the volume of air confined in A, B and C, and so corrects a defect existing in most instruments of this kind.

UNIVERSITY OF VIRGINIA.

## INSPECTION OF COTTON FOR USE IN THE MANUFACTURE OF GUNCOTTON.<sup>1</sup>

BY CHARLES E. MUNROE.

Received August 2, 1895.

WHEN converting cotton into guncotton by immersion in mixed acids, as practiced in the Abel process, it is essential that the cotton should rapidly absorb the acid for if the portion that is taken for immersion be but slowly absorbent, it is likely when but partly saturated to rise to the surface of the acid and on exposure to undergo the rapid decomposition technically called "firing." To secure the desired result the cotton should be free from oil, grease, and any protecting body. Their presence not only diminishes the absorptive power of the cotton but they, in common with the knots, tangles, cops, hulls, seeds, or similar foreign bodies, promote decomposition. It is a common practice to

<sup>1</sup> Read at the Brooklyn meeting.

use weaver's waste, or waste from the cotton gauze factories, in this manufacture on account of its cheapness and because it is found also that the thready form permits of ready handling in the hand-dipping and its compactness diminishes the amount of air which becomes entangled in the mass, as compared with that entangled in a similar mass of cotton "in the wool," and consequently the bouyancy of the mass is less.

Such waste necessarily becomes soiled with oil or grease, to a greater or less degree, during the carding and spinning, and it may contain besides knots, cops, tangles, and foreign bodies of various kinds, which latter are removed by means of the picker, while the oil and grease are removed by boiling with soda lye. Hence in determining the relative value of various samples of cotton offered for purchase, the relative amount of the grease, foreign bodies, and waste to be removed and of knots and tangles present, together with the general cleanliness of the sample, are to be considered.

Based on considerations such as these, the method of inspection is as follows :

1. Optical examination for color, cleanliness, presence of cops, knots, tangles, and foreign bodies, and for relative length and strength of fiber.

2. Odor.

3. Moisture, which is determined by drying a portion at 100° C. to constant weight.

4. Ether extract, which is determined by subjecting the weighed sample to the action of petroleum ether (boiling-point 50°-80° C.) in a Soxhlet extractor until the sample ceases to lose weight. The method of procedure is to expose the weighed sample in a light glass basket to ten automatic exhaustions, when it is removed, dried, and weighed. It is then returned to the extractor and subjected to five automatic exhaustions, when it is again dried and weighed. If it has lost weight by the last treatment the basket and contents are again returned to the extractor and exhausted three times and this treatment is repeated until the weight becomes constant.

The weight of the samples taken in the experiment varied between one and one and a half grams and the extractor had a

capacity of forty cc. for each automatic exhaustion. The ether extracts the oily matters in the cotton, both those which occur naturally and those which it has absorbed in the processes to which it has been subjected.

5. Soda-lye extract, which is determined by boiling the weighed sample for eight hours in a solution of sodium hydroxide of the same strength and in the same proportions as that used in the factory in the first boiling tub. For this purpose the waste, if in long bundles, is cut into pieces about one inch long, and ten grams of it placed in a beaker of about a half liter capacity, 104 cc. of a solution of caustic soda containing 17.305 grams to the liter (thirty-five pounds to 250 gallons of water) are poured upon it and the boiling carried on for eight hours, fresh water being added from time to time to keep the solution at constant volume. At the end of eight hours the liquid is poured off and the sample placed in a cotton filter, where it is squeezed and washed with hot water until the wash water gives no alkaline reaction. The sample is then dried to constant weight.

6. Ash, which is determined by placing from one to one and a half grams of the sample in a weighed platinum crucible pouring melted paraffin upon the mass, igniting it from the top, allowing it to burn slowly until the flame dies out and then igniting the residue to constant weight.

7. Rate of absorption of water. In making this test a sample of the material is thrown or dropped lightly on the surface of distilled water and the time between when it touched the surface and when (through absorption of the water by capillarity) it sinks to the bottom noted. One of the requisites for cotton suitable for making smokeless powder is that it shall sink in two minutes. In these experiments the cottons were tested not only in the condition in which they were received but also after treatment with ether; after drying for moisture, and after boiling with soda-lye; all being in the dry state. The vessel used varied in diameter from three to six inches, while the temperature of the water varied from 20° to 25° C. These differences or that of the size and form of the pellet seemed to produce no effect, but special attention must be paid to having distilled

water with a perfectly clean surface. With the same sample of cotton there were considerable variations in the time of sinking to the bottom of the vessel although the time of becoming thoroughly saturated so as to become submerged at the surface was fairly constant. The fact that the mass remained at the surface after saturation was found usually to be due to a bubble of air entangled in the mass which bouyed it up, or, less often, to a small portion of the mass being non-absorbent. This condition was evident on inspection as the non-absorbent portion of the sample remained opaque, while the absorbent portion appeared translucent. When the absorption failed to begin at once it usually did not take place at all, even after twenty-four to forty-eight hours exposure, or even when the whole mass was forcibly plunged beneath the water, in fact in these cases there seemed to be an actual repulsion between the water and the fiber. As what we seek to learn by this test is the relative rates at which the cottons tested will suck up the mixed acids during dripping, it would seem sufficient to note the moment at which they become thoroughly wet and submerged beneath the surface.

The detailed results obtained with five samples submitted at one time are as follows :

1. *Sample 1.*—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt and rust spots. Strong fiber.

*Sample 2.*—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt. Very strong fiber.

*Sample 3.*—Off white, yellowish tint. Long threads, freer from tangles than 1 or 2. Free from dirt. Strong fiber.

*Sample 4.*—White. Partly short threads and partly loose fiber as if picked. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few rust spots.

*Sample 5.*—White. Whole fibrous and wooly, as if picked, the fibers being not over an eighth of an inch in length. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few dark specks.



2. *Sample 1.*—Faint odor of oil.

" 2.—Very faint odor of oil.

" 3.—Marked odor of oil.

" 4.—Very faint odor of oil.

" 5.—Very faint odor of naphtha (?)

The percentages of moisture, ether extract, soda-lye extract, and ash, (3, 4, 5, and 6) are given in the following table:

Sample No.	Moisture.	Ether extract.	Soda-lye extract.	Soda-lye extract less moisture and ether extract.	Ash.
1.	4.93	0.97	9.16	3.26	0.86
2.	4.79	0.49	10.36	5.08	0.75
3.	5.17	1.20	9.26	2.80	0.80
4.	4.36	0.53	13.69	8.80	0.61
5.	4.69	0.09	7.58	2.80	0.40

7. The rates of absorption of water found was as follows:

Sample No.	Original condition of sample. Min. Sec.	After exhaustion with petroleum ether. Min. Sec.	After boiling in soda-lye. Min. Sec.	After drying for moisture determination. Min. Sec.
1.	∞	∞	$\left\{ \begin{array}{l} 2 \text{ } 00 \\ 1 \text{ } 00 \\ 2 \text{ } 00 \end{array} \right.$	∞
2.	∞	∞	$\left\{ \begin{array}{l} 2 \text{ } 00 \\ 1 \text{ } 00 \\ 1 \text{ } 40 \\ 50 \\ 3 \text{ } 30 \end{array} \right.$	∞
3.	∞	∞	∞	∞
4.	$\left\{ \begin{array}{l} 3 \text{ } 15 \\ 5 \text{ } 15 \\ 1 \text{ } 15 \end{array} \right.$	$\left\{ \begin{array}{l} 60 \\ 45 \end{array} \right.$	$\left\{ \begin{array}{l} 10 \\ 8 \\ 7 \\ 4 \end{array} \right.$	$\left\{ \begin{array}{l} 3 \text{ } 00 \\ 4 \text{ } 00 \\ 7 \text{ } 45 \end{array} \right.$
5.	∞	$\left\{ \begin{array}{l} 45 \\ 45 \\ 20 \\ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 10 \\ 4 \\ 4 \end{array} \right.$	∞

∞ No submersion after twenty-four hours' exposure.

The appearance of the ash and of the soda-lye after extraction are worthy of notice. In samples 1, 2, and 3, the ash obtained was of a light green color, the green portion being soluble in water, leaving a yellowish residue, which was insoluble. The ash of samples 4 and 5 was reddish. The color seemed to be due,

in each case, to iron, it being in the ferrous condition in the first three cases and the ferric in the last two. As the latter evidently have been bleached with chlorine, this treatment would naturally oxidize the iron.

Soon after boiling the lye with the cotton began, the former, which was colorless at the start, began to acquire a color which increased in intensity for some hours. In the case of samples 1, 2, and 3, the lye, when the operation was finished, was of a pale sherry wine color, No. 4 was of a port wine color, while No. 5 was of a deep sherry wine color.

From this examination the samples are divided into two classes, *viz.*: cop waste and short fiber, treated cotton. Samples 1, 2, and 3 being in the first class and samples 4 and 5 in the second.

The short-fibered cotton cannot be nitrated successfully with the usual appliances and the presence of chlorine is objectionable as the cellulose nitrates produced from such cotton cannot be washed neutral.

Of the cop wastes, which are adapted to our present methods of manufacture, sample 1 seems on the whole to be the best, though it is but little superior to sample 2.

From the observations made it was found that in eighteen samples of cotton waste—

The moisture varied from 3.38 to 8.40 per cent.

The ether extract from 0.00 to 7.10 per cent.

The soda-lye extract from 3.53 to 5.36 per cent.

The ash from 0.05 to 1.79 per cent.

The rate of absorption after soda-lye extraction from one second to over twenty-four hours.

A sample of cottonseed lint gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
6.16	2.35	28.54	4.83	∞

A sample of waste cotton gauze gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
7.37	0.50	3.89	.95	7 seconds.

The rates of absorption quoted are for samples dried after receiving the soda-lye treatment. As indicated above, observations were also made on the original sample and after treatment

with ether, both after drying. The highest rate was obtained after boiling with soda-lye; many samples being still non-absorbent after treatment with ether.

Treatment with the soda-lye even improved the absorbent power of the samples of "Absorbent Cotton" submitted for testing the rate being increased from three seconds for the dried, untreated cotton, to one second for that which had been treated.

Experiments were made on the absorptive capacity of the cotton, and in one case a six-gram sample of absorbent cotton was found to retain ninety-three grams of water or 15.5 times its own weight.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY  
No. 8.]

### REDUCTION WITH MAGNESIUM AMALGAM.

BY HERMANN FLECK AND LEWIS L. BASSETT.

Received August 21, 1895.

THE subject of neutral reducing agents has been taken up in a recent publication by J. B. Cohen and R. Ormandy.<sup>1</sup> The study of the same subject has been carried on in this laboratory during the past year. For this purpose magnesium amalgam, two per cent., was prepared in the following manner:

The required amount of mercury is placed in a small Hessian crucible and half covered with magnesium powder. The lid is put on loosely and the blast applied until a loud hissing noise begins. Once begun the reaction takes place by itself. This is repeated until the requisite quantity of magnesium powder has been added. A more uniform mass is obtained by boiling mercury in a hard glass tube, open at one end; then adding the magnesium in small quantities and shaking vigorously after each addition. The product is a silver white, crystalline, pasty mass which decomposes water with great energy and evolution of heat, and which upon exposure to air becomes covered with a black mass; probably a lower oxide of magnesium.

#### MAGNESIUM AMALGAM AND HYDROCYANIC ACID.

Two hundred cc. of ninety-six per cent. alcoholic solution of hydrocyanic acid containing eight grams of the acid were placed

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 1505.

in a liter distilling bulb connected to a condenser by a rubber tube. The condenser, by means of a long glass tube, led into a flask containing dilute hydrochloric acid, and this in turn was attached to a suction pump. After cooling in a mixture of ice and salt a small quantity of the amalgam was introduced into the neck of the distilling bulb, the cork replaced, and by a sharp jerk introduced into the liquid. When the theoretical amount of two per cent. amalgam had been introduced the contents were directly distilled into dilute hydrochloric acid evaporated to dryness, redistilled with addition of caustic soda into dilute hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. A small amount of ammonium chloride remained, produced by the action of hydrochloric acid upon the unconverted hydrocyanic acid.

The yield was fifteen per cent. 0.1122 grams methylamine platinichloride gave 41.08 per cent. platinum, the theory being 41.24 per cent. With more than the theoretical amount of amalgam a larger yield can surely be obtained.

#### MAGNESIUM AMALGAM AND BENZONITRILE.

Ten grams benzonitrile were dissolved in 200 cc. of ninety-six per cent. alcohol and twice the theoretical amount of amalgam added under the same conditions as above. The reaction product was filtered on a suction pump from the magnesium hydroxide formed and evaporated to dryness with hydrochloric acid, caustic soda added and extracted three times with ether. The ethereal solution was evaporated with hydrochloric acid to dryness and the residue extracted with absolute alcohol. There remained one gram of a crystalline substance melting under  $100^{\circ}\text{C}.$ , whose alcoholic solution immediately reduced platinic chloride. This substance, possibly of a hydride nature, will be further investigated.

#### MAGNESIUM AMALGAM AND ACETOPHENONE.

Ten grams acetophenone were dissolved in fifty cc. ether and somewhat more than the theoretical quantity of amalgam added. When the mass cakes, alcohol is added and then sufficient water to completely decompose the amalgam. Dilute hydrochloric acid is added to dissolve the magnesium hydroxide formed, and

the semi-crystalline mass extracted with ether, the ethereal solution evaporated to dryness, crystals formed freed from oily substance by washing with ligroin, and recrystallized from benzene.

Of the products theoretically possible, acetophenone pinacone, or diphenyl dimethyl glycol, forms large colorless prisms, melting at  $120^{\circ}$  C. The product obtained melts at  $120^{\circ}$  C., and in every particular corresponds to the above. The yield was excellent.

It is our intention to further pursue the investigations with nitriles, ketones, oxynitriles, and amido-nitriles.

UNIVERSITY OF PENNSYLVANIA.

## TWO DEFINITE CARBIDES OF IRON WITH CHROMIUM (MOLYBDENUM AND TUNGSTEN).

BY JAMES S. DE BENNEVILLE

Received September 6, 1895.

A PREVIOUS paper<sup>1</sup> described in detail the results of a chemical examination of some ternary alloys of iron with chromium, molybdenum, and tungsten. In the course of the experiments there described two definite carbides were separated and it is proposed to give additional details obtained later. The physical description of the crystals is taken from Professor F. Lynwood Garrison's discussion of the paper cited.<sup>2</sup> The alloys described were made by taking pairs of the elements: tungsten chromium irons, molybdenum chromium irons, and molybdenum tungsten irons. The proportions taken were not based on equal weights but on quantities taken in the ratio of the atomic masses of the constituents. They were 1:1, 5:1, and 1:5. A lump of cast iron weighing fifty grams was imbedded in the mixture and melted, a white heat being maintained for an hour. The aggregations to be described were found in the chromium alloys and only in the two alloys (Nos. II and V) in which chromium was the predominant metal. These two alloys showed well individualized crystals differing in form and reactions from the matrix in which they were imbedded.

<sup>1</sup> Iron and Steel Institute, May meeting, 1895.

<sup>2</sup> *Ibid.* I take this opportunity of expressing my indebtedness to Professor Garrison, through whose kind offer I was enabled to present this paper, to the council of the Institute.

Berthier and also Percy<sup>1</sup> have noted the presence of needle-shaped crystals in ferrochromium and in chromium steels. Further details are not given. Behrens and Van Linge, in a recent paper, have described at length the physical and chemical properties of segregations in ferrochromium. On treating the alloy with acid they obtained bayonet or rod-shaped crystals, three to four millimeters in length, a few being eight to ten, non-magnetic, of hardness 7.5. The composition, however, varied with the ferrochromium from which they were obtained; ferrochromium with 13.8 per cent. chromium, eighty-one per cent. iron, and five and one-half per cent. carbon, giving the compound  $\text{Cr}_7\text{Fe}_3\text{C}_8$ , whereas with fifty per cent. chromium, the composition was approximately  $\text{Cr}_7\text{FeC}_8$ . They point out the relation of the first compound to  $\text{Fe}_3\text{C}$ , chromium replacing a part of the iron, and consider that chromium forms "double carbides less soluble in iron than the ferrocabides, at the same time facilitating the crystallization of the latter."<sup>2</sup>

Considering the marked development of the segregations in the ternary alloys it appears to me doubtful whether they are to be referred, as to origin, to the iron carbides. The prismatic form is not a dominant one with the iron carbides, although it is found under certain conditions. Howe, citing Sorby, notes three successive crystallizations in hard cast-steel. I quote him in *extenso*: he says, "First we have the large prismatic columnar crystals, normal to the cooling surface, and conspicuous on fracture. They apparently represent the first crystallization, be it of hardenite, be it of the hypothetical mother-of-pearlyte, which in this case has expelled the excess of cementite present, distributing it as an elongated meshwork between the crystals. Secondly, these columns or crystals are chiefly composed of groups of pearlyte, disposed with little or no relation to the columnar structure, indeed shooting from one column into another, and apparently formed from the substance of the primary crystals of a second crystallization. Finally, by a third crystallization, each of the individual members of the radial

<sup>1</sup> Percy, *Iron and Steel*, p. 186. Berthier from Percy not the original.

<sup>2</sup> *Recul trav. chim. Pays-Bas.*, 13, 155-181. From the abstracts in *J. Soc. Chem. Ind.*, 14, 275, 1895, and *J. Chem. Soc.*, 64, 452, 1894.

groups of pearlyte has split into parallel layers of cementite and ferrite, which apparently occupy the space previously occupied by a simple undivided crystal." Again, "the exterior columnar structure is clearly due to the rapid escape of heat from the shell of the ingot into the mold. We may suppose that the metal naturally tends to crystallize in equiaxed grains: that there is a struggle between this tendency and the tendency to crystallize in indefinitely long prisms which the rapid cooling sets up. As the walls thicken and the flow of heat outward slackens, the prismatic tendency weakens: the sudden transition from the prismatic to the equiaxed formation suggests that no resultant, no compromise is possible, so that from the moment when the equiaxial tendency outweighs the prismatic it reigns alone, as if its rival were not."<sup>1</sup> This is the only mention of prismatic structure in ordinary carbon steel that I find in the "Metallurgy." If the intense hardness of ferrochromium, ferrotungsten, and ferromolybdenum is to be ascribed to the conversion of the carbon present into hardening carbon and its retention in that form—although from the researches of Riche and especially of Moissan this hardness can just as well be attributed to carbides of chromium, tungsten, or molybdenum—the alloys under discussion can be justly compared to hard cast-steel containing a large excess of carbon and the prismatic form of the crystals in II and V could be attributed to a structure found in such steel as described above. However, the conditions are by no means identical. The crystals in II and V are present throughout the mass forming a network with the interstices filled in by the equiaxial granular material. There is no line where the equiaxial tendency has overcome the prismatic and so sharply differentiated the alloys into an external prismatic shell surrounding an interior of equiaxed grains. Also, the crystals show a marked increase in density as compared with the granular material and the alloys in which they are found differ in hardness from the rest of the series. In fact, the crystals give every evidence from their sharpness of outline of having a higher freezing-point and as having separated out from the mass of the alloy at a time when it was not liquid enough to effect their

<sup>1</sup> Metallurgy of Steel, p. 182, 183.

segregation into any one portion of the alloy, but liquid enough to secure their own crystalline form at the expense of compounds crystallizing later. For when a mass of iron is allowed to cool uniformly, from the resultant structure it would appear that the constituent compounds have freezing points not so far removed from each other as to effect the segregation of any one of them into a part of the mass. This has no reference to the microstructure of iron and steel in which the compounds identified appear to be somewhat unstable in nature, passing readily from one form to the other even by cold working. The columnar structure is only stable under the limited conditions existing for its formation and by slight alteration of the method of cooling or of working passes readily into other forms. Also, the columns are often distinctly a mere structural arrangement of the granular material with radial lines forming prismatic aggregations in which the granular components are distinctly manifest. There is in the micro structure of steel a compound to the development of which might be attributed the prismatic and needle-like form when found in iron alloys. This has been described by Osmond<sup>1</sup> and named by him martensite. It is found in steel of 0.45 carbon heated to 825° and tempered at 720° in a cooling mixture of -20°. It occurs "in groups of needles or rather of rectilinear fibers lying parallel and separated or not by a granular or vermicular filling." From the grouping of three systems of fibers respectively parallel to the three sides of a triangle he regards them as crystallites of the cubical system. In the absence of any other source the form of the prismatic needles found in ferrochromium and in these tungsten chromium irons (II) and molybdenum chromium irons (V) could be attributed to the development of the microstructural element, to the fixation of the prismatic columnar structure, or to the rod-shaped fiber structure of Abel's carbide  $\text{Fe}_3\text{C}$ . As to the two first, in despite of their instability and the absence of any boundary line between the prismatic and granular formations, it seems to me better to attribute the form to the carbide of chromium isolated by Henri Moissan.<sup>2</sup> This carbide, of formula  $\text{CCr}_3$ , he describes

<sup>1</sup> Bull. de la Soc. d'Enc. pour. l'Ind. Nat., May, 1895.

<sup>2</sup> Bull. Soc. Chim. Paris, 11, 1016, 1894.



as forming needles one to two cm. in length lining the cavities found in the melt. He also isolated a carbide  $\text{C}_3\text{Cr}$ , occurring in brilliant lamellae. Of the two the lamellar carbide was the harder, scratching topaz but not corundum, whereas the prismatic carbide scratched glass readily, but quartz only with difficulty. Both carbides were very stable compounds and were chemically inert. The crystals found in the ternary alloys were confined to the high chromium compounds in which the ratio of chromium to tungsten or molybdenum was as five to one. The alloys, II and V, were much softer than the other alloys, which would be the case if hardness is dependent on the carbide of chromium present. For comparison, Table I gives the composition of the series of alloys.

If now the prismatic segregations in ferrochromium be compared it will be found that, with the exception of the compound  $\text{Fe}_3\text{Cr}_3\text{C}_3$ , chromium is the dominant constituent in the carbide. For example :

TABLE II. SEGREGATIONS IN FERROCHROMIUMS.

	B. and Van L. $\text{Fe}_3\text{Cr}_3\text{C}_3$	B. and Van L. $\text{FeCr}_2\text{C}_2$	V. Analysis 1 $\text{Fe}(\text{CrMo})_5\text{C}_4$	V. Analysis 2. $\text{Fe}(\text{CrMo})_5\text{C}_4$	II. $\text{Fe}(\text{CrW})_5\text{C}_4$	II B. $\text{Fe}(\text{CrW})_5\text{C}_4$
Iron .....	0.8100	0.3030	0.4639	0.4650	0.4724	0.4723
Chromium ..	0.1380	0.5671	0.4623	0.4606	0.3542	0.3682
Molybdenum ....	....	....	0.0201	0.0194	....	....
Tungsten ...	....	....	....	....	0.1139	0.1007
Carbon .....	0.0550	0.1299	0.0553	0.0559	0.0595	0.0599

$\text{Fe}_3\text{Cr}_3\text{C}_3$ , on the contrary, could fairly be classed as derived from an iron compound— $\text{Fe}_3\text{C}$ . This compound, isolated by Abel and subsequently by Muller, is described as a dark-grey residue; Osmond and Werth obtained it in the form of bright plates; Behrens and Van Linge treating Dannemora iron, obtained it as bright spangles and rods; and Arnold and Read obtained it in two forms, as bright silver plates and as a grey black powder in microscopic granules.<sup>1</sup> The segregations in the ternary alloys are to be compared with the "brilliant white radial needles" described by Behrens and Van Linge and which

<sup>1</sup> Abel—Proc. Inst. Mech. Eng., 1895, p. 30; Muller—Stahl und Eisen, No. 5; Osmond and Werth—Annales des Mines 1895; Behrens and Van Linge—as cited, 1894; Arnold and Read—*J. Chem. Soc. Trans.*, 65-788, 1894. Also Ledebur Jour. Iron and Steel, Inst. 1893, II. 53. The quotations following are from the abstract of Behrens and Van Linge's paper.

TABLE I. COMPOSITION OF THE ALLOYS. *J. Iron and Steel Institute, I, 1895.*

ALLOY	I	II	III	IV	V	VI
Total carbon.....	0.0317	0.0299	0.0311	0.0323	0.0312	0.0323
Carbon evolved by hydrochloric acid.....	0.0172	0.0272	0.0172	0.0174	0.0284	0.0130
Carbon in hydrochloric acid residue.....	0.0195	0.0225	0.0184	0.0219	0.0228	0.0193
Carbon in nitric acid residue.....	none	Table VIII	none	none	Table VIII	none
Silicon evolved by hydrochloric acid.....	0.0033	0.0142	0.0072	0.0075	0.0055	0.0022
Silicon in hydrochloric acid residue.....	0.0193	0.0083	0.0130	0.0103	0.0119	0.0051
Phosphorus evolved by hydrochloric acid.....	0.0019	0.0025	0.0012	0.0013	0.0020	0.0003
Phosphorus in hydrochloric acid residue.....	0.0009	0.0007	0.0003	0.0006	0.0005	0.0000
Manganese.....	0.0004	0.0043	0.0049	0.0013	0.0027	0.0004
Sulphur.....	—	—	—	—	—	—
Chromium.....	0.0846	0.1207	0.0211	0.0802	0.2257	0.0485
Tungsten.....	0.3382	0.0440	0.2125	—	—	—
Molybdenum.....	—	—	—	—	—	—
Iron.....	0.5197D	0.7154D	0.7987D	0.1184	0.0715	0.3965
Specific gravity.....	11.010	7.935	10.257	0.7531	0.6470D	0.8999
Formula.....	$\text{Fe}_{10}\text{Cr}_4\text{W}_6$	$\text{Fe}_{10}\text{Cr}_{11}\text{W}$	$\text{Fe}_{10}\text{Cr}_7\text{W}_5$	$\text{Fe}_{10}\text{Cr}_{10}\text{Mo}_4$	$\text{Fe}_{10}\text{Cr}_{10}\text{Mo}_4$	$\text{Fe}_{10}\text{Cr}_8\text{Mo}_7$
Condensation from composition difference.....	2.031+	0.453+	1.869+	0.089+	0.054—	0.963+

ALLOY	VII	VIII	IX	Cast iron used.	Chromium for steel.	Tungsten for steel.
Total carbon.....	0.0335	0.0289	0.0290	0.0331	0.0773	0.0343
Carbon evolved by hydrochloric acid.....	0.0162	0.0126	0.0147	0.0039	—	0.0014
Carbon in hydrochloric acid residue.....	—	—	—	—	—	nitrogen
Carbon in nitric acid residue.....	—	—	—	—	—	—
Silicon evolved by hydrochloric acid.....	0.0173	0.0163	0.0153	0.0202	—	—
Silicon in hydrochloric acid residue.....	0.0073	none	none	0.0286	—	—
Silicon evolved by hydrochloric acid.....	0.0097	0.0184	0.0023	0.0030	total	total
Phosphorus evolved by hydrochloric acid.....	0.0014	0.0067	0.0040	0.0194	0.0144	0.0039
Phosphorus in hydrochloric acid residue.....	0.0006	0.0017	0.0018	0.0020	total	total
Manganese.....	0.0003	0.0013	0.0006	0.0004	0.0012	trace
Sulphur.....	—	0.0019	0.0034	0.0071	trace	—
Chromium.....	—	—	—	0.0003	—	—
Tungsten.....	0.1471	—	—	—	0.8995	—
Molybdenum.....	0.0949	0.1940	0.3666	—	—	0.9593
Iron.....	0.7012	0.1346	0.8379	—	—	—
Specific gravity.....	11.154	0.6086	0.6189	0.9347D	—	—
Formula.....	$\text{Fe}_{10}\text{Mo}_4\text{W}_4$	$\text{Fe}_{10}\text{Mo}_4\text{W}_5$	$\text{Fe}_{10}\text{Mo}_4\text{W}_{17}$	7.474	0.0079	0.0007
Condensation from composition difference.....	2.898+	2.942+	3.438+	—	5.103	15.175
				—	—	—

D=by difference.

are characteristic of ferrochromium, attaining a very marked development which places them entirely outside the category of micro or sub-micro structure. I am in doubt as to whether the formula  $\text{Fe}_3\text{Cr}_3\text{C}_3$  is meant to represent the needles, for this compound is described as "a coarse brownish grey lustrous powder, made of small bars, of which many are three to four mm. in length." The data are confessedly very scanty but against the iron derivation of the needles is to be placed the three compounds found in the ternary alloys whose constancy can hardly be ascribed to the constituent tungsten or molybdenum, metals chemically to be classed with chromium; and the existence of Moissan's carbide  $\text{Cr}_3\text{C}$ , an analogous compound. This is more clearly understood from Professor Garrison's description given later. That, however, the constitution of such compounds would be dependent on the composition of the mixture and would only be fairly constant within certain limits can be readily understood, as, for example, with double salts crystallizing in varying proportions; and hence when the iron becomes an unimportant factor in the composition of the alloy its influence would correspondingly wane in the compound crystallizing from the mixture, and vice versa. It is to be noted, moreover, that very little is known of the valence or combining power of the elements in metallic alloys and not only is this lacking for iron and chromium, but if the composition of the crystals is dependent on the composition of the alloy and the temperature at which they separate there may also be an alteration in the ratio in which iron and chromium combine, for valency may well be dependent on the temperature. Note that alloy II contains 12.07 per cent. of chromium but has a much greater content of chromium in the separated crystals than the compound of formula  $\text{Fe}_3\text{Cr}_3\text{C}_3$ .

The separation of the crystals from the granular material was readily effected by the comparatively slight action of nitric acid which left the crystals as residue intermixed with a little silica. This was volatilized as silico-fluoride and after washing with water and subsequently with ninety-five per cent. alcohol the crystals were obtained free from impurity. Their reactions show them to be chemically very inert compounds. As stated, they are but little attacked by nitric acid, strong or dilute.

Hydrochloric or hydrofluoric acid does not attack them. Strong sulphuric acid slowly decomposes them leaving a black residue which still retains the form of the crystals. The solvent is useless as a means of analysis. By themselves the crystals are attacked but slowly by strong aqueous solution of bromine or of iodine and only on heating. However, in the residue obtained by treating the alloy with these reagents no trace of the crystals could be observed, using a lens magnifying fifty diameters. With reflected light the residues showed granular masses of irregular shape with brilliant metallic luster. From the mode of occurrence of the crystals in the alloy they could hardly have been absent from the samples examined. At a red heat chlorine, bromine, and iodine readily decompose them, but their analysis is best effected by fusion with an oxidizing mixture of sodium carbonate and saltpeter with addition of caustic soda.

Professor Garrison, in his discussion,<sup>1</sup> gives the form and dimensions of the crystals as follows: "I have examined under the microscope the segregations obtained from alloys II and V and find them to consist of well developed prismatic hexagonal crystals, more or less corroded by the nitric acid solvent. I was not able to detect any of the crystals with pyramidal terminations; most of them appeared to have been broken, leaving ragged ends, as would be observed in Figs. 1 and 2. The general appearance of the crystals from the different alloys is similar. Those from II averaged 0.03 to 0.04 of an inch in length, and 0.003 of an inch in diameter; those from V were 0.03 to 0.04 in length and 0.005 of an inch in diameter. The aspect of the crystals under a magnification of thirty-five diameters is well shown by the micro-photographs; Fig. 1 being from alloy II, and Fig. 2 from V, I was able to detect a slight difference in color between the two varieties when they were heaped in masses and held in the proper light. II had a decided yellowish metallic luster; V a dark steel-grayish-blue color and luster. The slight difference in thickness was not appreciable to the naked eye, neither would the color or luster be apparent to a casual observer. I experienced some difficulty in making the specific gravity determinations of these crystals, owing to

<sup>1</sup> Iron and Steel Institute, May meeting, 1895.

the extremely small quantities. On the whole, I think those mentioned are nearly correct, although that of II might be a light one." Of II specific gravity is 12.80; of V 7.473 (Garrison).<sup>1</sup>

The analytical results obtained were :

*Alloy V.—Ferromolybdenumchromium Carbide.* The analysis was made as follows : Half a gram of pure crystals were fused with the oxidizing mixture with addition of caustic soda. The melt was cooled, lixiviated in water, and the solution containing chromate and molybdate filtered from the residual ferric hydroxide. The solution was acidified with hydrochloric acid and boiled to dryness with addition of alcohol to ensure reduction of the chromic salt. The residue was then dissolved in a little dilute hydrochloric acid, diluted and brought to boiling. Chromium was precipitated by ammonia in excess, the boiling being continued for at least half an hour. The precipitated chromic hydroxide was filtered off, washed twice with hot water, dissolved in dilute hydrochloric acid, and reprecipitated by ammonia. This solution was filtered, the filtrate being added to the first but not the washings. The chromic hydroxide was now thoroughly washed by boiling up with water, decanting, finally throwing on the filter, and washing with boiling water. It was then dried, ignited, and weighed as  $\text{Cr}_2\text{O}_3$ . In analysis 1 (table II) the filtrate containing the molybdenum was boiled until the odor of ammonia had to a great extent disappeared. The solution was then acidified with sulphuric acid, poured into a separatory funnel containing zinc and, after reduction, titrated with permanganate (Pisani's method). In analysis 2 the molybdenum was determined gravimetrically. The ferric hydroxide was examined for silica but the quantity found checked closely with that present in the alkali salt used for fusion. After removal of platinum, iron was converted to sulphate and titrated in acid solution by permanganate. The chromic oxide was fused with bisulphate and the solution examined for phosphorus with nega-

<sup>1</sup> In some experiments carried out by Professor Garrison and myself with highly phosphoric titaniferous pig iron, prismatic needles were obtained lining the cavities and blow-holes. Their form could not be made out with certainty but they were well developed and in no sense belonged to the micro structure of the alloy. They have not yet been isolated. The prismatic form is of frequent occurrence in Ferromanganese.

tive results. If silicon or phosphorus were important constituents of the crystals they would readily be detected in a half gram sample. The carbon of analysis 1 was determined by direct combustion of the crystals with the lead and potassium chromate mixture. The carbon of 2 was determined by combustion of the residue obtained after first decomposing in chlorine at a red heat.

TABLE III. FERROMOLYBDENUMCHROMIUM CARBIDE.

	Analysis 1. Atomic ratio.		Analysis 2. Atomic ratio.	
Iron .....	0.4639	0.828	0.4650	0.830
Chromium .....	0.4623	0.882	0.4606	0.879
Molybdenum.....	0.0201	0.021	0.0194	0.020
Carbon.....	0.0553	0.461	0.0559	0.464

No manganese, silicon, or phosphorus were present. These results give the ratio  $\text{Fe}:\text{CrMo}:\text{C}::1.79:1.95:1$ , or formulated  $\text{Fe}_2(\text{CrMo})_2\text{C}_2$ . To this compound I give the name Wahlite, from Dr. William H. Wahl, well known for his valuable contributions to metallurgy.

Alloys II and II B. — *Ferrotungstenchromium Carbide*. In addition to the alloy (II) described in the first paper, a second alloy (II B) was made using 200 grams of iron in the melt instead of fifty. The object in doing so was to determine whether change in composition of the melt had any effect on the composition of the resultant crystals. The quantity of crystals obtained for analysis II was small. Iron, chromium, and tungsten were determined after purifying by nitric acid one gram of the original material. The residue was then analyzed and the calculations made to 100 per cent. For analysis II B abundant material was available. Considering the small quantities available for the first analysis the agreement is satisfactory. Comparing with alloy V it would appear that the ratio of chromium to iron is not the same in the two alloys. Tungsten and molybdenum probably play the same rôle as chromium and replace it perhaps in varying quantities. The analysis was made by decomposing the crystals as with alloy V. The solution containing tungstate and chromate was acidified with hydrochloric acid, alcohol added, and evaporated to dryness. The residue was taken up in dilute hydrochloric acid and an equal bulk of alcohol added.

The tungstic acid was filtered off, dissolved from silica by ammonia, the solution evaporated, and tungsten determined as  $\text{WO}_3$ . The filtrate containing chromium was brought to boiling and chromium hydroxide thrown down by ammonia. Alloy II, as obtained in original sample, contained iron 0.0423, chromium 0.0317, tungsten 0.0102. The analytical results gave:

TABLE IV. FERROTUNGSTENCHROMIUM CARBIDE.

	Alloy II.	Atomic ratio.	Alloy II B.	Atomic ratio.
Iron.....	0.4724	0.843	0.4723	0.843
Chromium .....	0.3542	0.676	0.3682	0.702
Tungsten .....	0.1139	0.060	0.1007	0.054
Carbon.....	0.0595	0.496	0.0599	0.494

No manganese, silicon, or phosphorus was present in II B. These results give the ratios:

Alloy II. Fe : CrW : C :: 1.69 : 1.49 : 1, or formulated  $\text{Fe}_2(\text{CrW})_2\text{C}_3$ .

Alloy II B. Fe : CrW : C :: 1.73 : 1.53 : 1, or formulated  $\text{Fe}_2(\text{CrW})_2\text{C}_3$ .

Carbon in both cases was determined by direct combustion of the crystals. To the compound I give the name Garrisonite, from Professor F. Lynwood Garrison, a valued contributor to the study of the microstructure of iron and to its metallurgy. Alloy II B contained, chromium 0.1070, tungsten 0.0871.

## ON THE POSSIBILITY OF THE OCCURRENCE OF HYDROGEN AND METHANE IN THE ATMOSPHERE.<sup>1</sup>

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BY FRANCIS C. PHILLIPS.

WHATEVER may have been the process by which organic remains have in the course of time been caused to yield gas and petroleum, a considerable portion of the gas evolved in the early stages of decay must have escaped into the atmosphere before the burial of such remains under sedimentary deposits, and the consequent imprisonment of the more volatile products could have occurred. This would have been the case if, as in the view of the older geologists, the source of gas and oil is to be looked for in the slow decomposition, at low temperatures, of

<sup>1</sup> Read at the Springfield meeting.

masses of seaweeds as they were gradually buried under accumulating sediments. It would have occurred likewise if, according to Engler's hypothesis, gas and oil have come from the distillation of animal remains under pressure of overlying sediments and at a gentle heat.

For a long interval of time must have elapsed between the commencement of decay and the final burial of such remains under marine deposits, of sufficient thickness and compactness, as to cause the retention of the hydrocarbons until the sediments became consolidated into rock.

In a paper upon the origin of natural gas<sup>1</sup> I have called attention to the great difference in the nature of the changes which may occur in organic remains submerged under water and protected from atmospheric influences. The early stages of the decay are rapid, and much hydrogen may be produced. The later stages are more gradual, and methane may be a chief product of the decay. At the beginning of the process the cell contents are chiefly concerned in the change. Even if buried under deep sediments the tumultuous nature of the gas evolution must cause the gas bubbles to break through and escape from dense masses of clay and sand.

The following experiment was described in the paper cited: A quantity of a seaweed was allowed to decay under water in an apparatus so constructed that any gas produced could be collected over mercury. Rapid decomposition soon set in and continued for ten days, when the evolution of gas apparently ceased, having become much retarded towards the end. In all 803 cc. of gas were collected. Analyses were made of the first portion of 300 cc., of a second portion of 300 cc., and of a third portion of 203 cc. The results are tabulated below:

	First portion.	Second portion.	Third portion.
Carbon dioxide.....	18.23 per cent.	32.47 per cent.	53.44 per cent.
Carbon monoxide..	0       "	0       "	0       "
Ethylene .....	0       "	0       "	0       "
Methane.....	0.30   "	0.28   "	0.08   "
Hydrogen.....	62.24   "	48.97   "	42.02   "
Nitrogen.....	19.23   "	18.28   "	4.46   "
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00



The temperature during the experiment did not exceed 20° C.

The same apparatus was kept in position for two and one-half years after the above experiment was made. During this time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 cc. of gas had collected. This was found to consist of methane.

Frankland & Jordan<sup>1</sup> found that grease left to decay under water, air being excluded, evolved gas of the following composition :

	In 3 days.	In 3 days.	In 4 days.
Carbon dioxide.....	84.63	87.66	84.41
Oxygen.....	0.13	....	....
Hydrogen.....	6.90	8.75	9.17
Other combustible gases .....	2.51	0.71	0.27
Nitrogen.....	5.83	2.88	2.15

I have examined gas collected from swamps in many localities. Gas samples have been taken from streams having muddy bottoms and in which vegetable remains had accumulated. Carbon dioxide, nitrogen and methane are usually found in shallow swamps. In deeper swamp waters, where masses of vegetable debris of greater thickness occur, hydrogen is often found in small quantities mixed with carbon dioxide, nitrogen and methane.

According to the hypothesis of Mendeleeff natural gas and petroleum have been produced by the action of steam at high temperatures upon the metallic compounds of carbon.\* The general result of experiments upon the action of steam upon the heated carbides of iron, manganese and other metals, has been to show that in all such cases there is produced mainly hydrogen mixed with relatively small quantities of hydrocarbons. It is found, however, that the natural gas which flows from the wells of Pennsylvania, New York, West Virginia, Ohio, and Indiana, consists mainly of methane with small quantities of other hydrocarbons, but does not contain free hydrogen. Hence if we accept the hypothesis of Mendeleeff we must suppose that the natural gas, now flowing from the earth in such vast quantities, represents the diminished residue of a much larger volume

<sup>1</sup> J. Chem. Soc. (Lond.) 1883, p. 295.

\* Mendeleeff: Principles of Chemistry, 1, 365.

of gas from which the free hydrogen has escaped through the overlying rocks. Whatever view is adopted as to the origin of natural gas there seems to be good reason to believe that considerable volumes of hydrogen and of gaseous paraffins have found their way into the atmosphere, and that the process has been continuous since early geological times.

Evolution of carbon dioxide from organic remains is merely one stage in a cycle of changes. The carbon dioxide present in the atmosphere parts with its carbon to growing plants. They, in their turn, yield back carbon dioxide as they die and decay. On the other hand each bubble of hydrogen and of methane, once set free at the earth's surface, probably escapes unoxidized and unabsorbed to ascend into the higher strata of the atmosphere.

Of all the forms which hydrogen and carbon can assume in nature, free hydrogen and methane are among the most stable and unalterable as regards all influences at the earth's surface. Their slight solubility in water protects them still further from oxidation.

In the natural gas regions gas bubbles are easily produced by stirring up the sediments at the bottom in streams, ponds and rivers. This is not only the case where decaying vegetation occurs, but in streams flowing over gravel and pebbles where no decay is in progress. The loose gravel appears merely to arrest temporarily the gas on its way out from the earth and renders it visible as it escapes in bubbles through the water. If the gas accumulated under gravel and sand in streams be dislodged by stirring it is usual to find that, in a day or two, or even after a few hours, it has again collected in considerable quantity. Constant agitation of the gravel seems not to diminish the amount of the gas flow.

Such emanations of gas are common in Western Pennsylvania and Western New York, in regions where the occurrence of hard rock directly below the gravel bed of a stream precludes the supposition that the gas has resulted from the decay of recently buried tissues. It is probable that the gas which is continually accumulating in such situations is derived from great depths, that its presence is the result of a slow process of diffusion from

below, which only terminates as the gas enters the atmosphere, and that it constitutes a considerable portion of the natural gas which was stored originally in the rocks.

The feebly luminous flame produced by this gas distinguishes it from the nitrogen, which so frequently collects in the sands of river beaches in regions of constant fluctuations of water level due to tides, and where organic remains are abundant.

In the latter case the air penetrating the sand at low tide parts with its oxygen to the decaying matter, and as the tide rises again the residual nitrogen is expelled in bubbles under the pressure of the advancing water, while the carbon dioxide formed is retained in solution.

Gas collected from the gravel bottom of a stream flowing into the Ohio river near Sewickley, Pa., was found to have the following composition :

	Per cent.
Methane .....	93.06
Nitrogen .....	6.70
Carbon dioxide .....	0.24
	<hr/>
	100.00

There is no reason to suppose that the diffusion of gas from the earth into the atmosphere is confined to surfaces covered by water, although it can only be made visible by the formation of bubbles in water.

It is no doubt continually in progress in regions of Devonian and carboniferous rocks.

This slow diffusion of gas from the earth into the atmosphere has occurred since early geological times and in regions where erosion has finally carried away whole systems of sedimentary rocks, liberating the imprisoned hydrocarbons by slow degrees. The gas thus escaping from within the earth's crust is added to that which is derived from recent decay on the surface; and probably forms no inconsiderable part of the total quantity carried continually into the atmosphere.

Hydrogen in a limited volume of air follows the well-known law of diffusion, mixing completely with the air.

Should a large mass of hydrogen enter the earth's atmosphere, the case would be different. Hydrogen, while it would diffuse

laterally with the air, would tend to accumulate in the upper strata on account of the great difference between its specific gravity and that of the constituents of the air. Ferrel,<sup>1</sup> has fully discussed the hypothetical case of the occurrence and arrangement of a very light constituent in the atmosphere, "Where the relative densities of the constituents regarded as independent atmospheres, would be nearly the same at the different altitudes, as in the case of oxygen and nitrogen, a constant agitation of the whole may keep them so mixed up that the proportions are nearly the same at all altitudes; but, in the case of a very rare constituent, the tendency would be for it to rise up so far above all the others that it could not become mixed up with them except in the lower strata, and at a considerable altitude it would be the only sensible constituent unaffected by the agitation of the comparatively much denser constituents which would exist, only sensibly lower down, near the earth's surface."

If the presence of hydrogen is ever positively detected in the atmosphere, it must be looked for in air samples collected as far away from the earth's surface as possible.

An experimental demonstration of the presence or absence of hydrogen in air, would be of great interest if the method to be employed were certain as regards its results. Existing methods for the detection or determination of hydrogen when present in traces, are not satisfactory.

After many trials, I have devised a method for the detection of traces of free hydrogen in a gas mixture. The method consists, briefly, in passing the gas over anhydrous palladium chloride contained in a glass tube. Free hydrogen reduces this salt at once, and in the cold, being converted into hydrochloric acid, which is recognized by passage through a silver nitrate solution.

Having in palladium chloride a reagent of extreme delicacy for free hydrogen, it seemed to be of interest to attempt a test for hydrogen in air, and in order to avoid as far as possible, all danger of impurities from local conditions at the earth's surface, some experiments were tried on Mount Washington, New Hampshire, during August, 1892.

<sup>1</sup> Annual Report of the Chief Signal Officer of the Army for 1885, pt. 2, p. 41.

The elevation of Mount Washington, nearly 7000 feet, did not justify the belief that upon its summit strata of air materially different from those at sea level could be reached, but there was the undoubted advantage of greater purity and freedom from local contamination.

By permission of Mr. Mark Harrington of the U. S. Agricultural Department, a room in the Weather Observer's building on the mountain, was used for the purpose.

I desire here to express my appreciation of the courtesy shown by Mr. Harrington and also by Mr. Mitchell in charge of the station, in affording facilities for the work.

Details of the work are omitted, as the results of two very carefully conducted experiments were negative, and therefore did not lead to a definite conclusion.

It may be suggested that ozone, by reason of its great oxidizing power, would tend to prevent the accumulation of combustible gases in the upper atmosphere. Oxygen is well known to derive its active properties from the influence of the electric discharge.

Ozone may be produced locally in considerable quantity as a result of violent electrical disturbances in the atmosphere. Much of the ozone thus formed probably expends its power in oxidizing atmospheric nitrogen to nitrous and nitric acid.

Ozone has a specific gravity much greater than oxygen, and would, consequently, tend to descend rather than to rise to the outer limits of the atmosphere. While the production of ozone must occur at points remotely distant and at considerable intervals of time, the evolution of hydrogen and methane at the earth's surface is continuous. Moreover, thunderstorms only occur during a brief portion of the year in temperate climates, and are unusual at all times in far northern latitudes.

In view of these facts it seems improbable that ozone can be considered likely to materially retard an accumulation of the lighter gases, hydrogen and methane, in the upper atmosphere.

Hydrogen and methane are not oxidized by prolonged contact with a two per cent. solution of hydrogen peroxide at 20° C.

It is true that the upper air may contain nitrous acid. Paper coated with potassium iodide and starch was found to be rapidly turned purple when exposed on Mount Washington. Free

hydrogen is, however, not oxidized by fuming nitric acid<sup>1</sup> and it is hardly likely that nitrous acid, in the highly diluted condition in which it must be looked for in air, could cause an oxidation of hydrogen.

Meyer<sup>2</sup> and Askenasy found that on exposure to bright sunlight, a mixture of oxygen and hydrogen suffered no change. Combination did not occur even on exposure of the gas to a temperature of 600° C.

Meyer and Seubert<sup>3</sup> have shown that under highly reduced pressure combination does not occur in a mixture of oxygen and hydrogen under the influence of the electric spark. Experiments with mixtures of various hydrocarbons with oxygen, led to similar results. The minimum pressures at which the electric spark caused an explosion, were about one-tenth of an atmosphere in the case of hydrogen, and one-sixth of an atmosphere in the case of methane. In earlier times Humphrey Davy was led to similar conclusions as regards the explosion of rarified gas mixtures.

Although the minimum pressure at which chemical union would occur, may vary with the character of the discharge, it may be asserted that electrical disturbances are less likely to influence the oxidation of these combustible gases in the higher atmosphere where they must be looked for, if present in the atmosphere at all.

Methane and hydrogen possess under all conditions, great resistance toward oxidizing agents, and, once set free in air, it is questionable whether either gas could undergo any change by which it might be wholly brought back within the sphere of reactions produced by organic life, or by oxygen. Ferrel has suggested that the hydrogen of the sun's atmosphere may form merely an outer layer, resting upon much denser gases below.<sup>4</sup> It is possible, at least, that such an arrangement exists in the earth's atmosphere.

It seems desirable that tests for hydrogen and methane in air, should be made at still greater altitudes in order that more defi-

<sup>1</sup> Winkler: *Ztschr. anal. Chem.*, 1889, 269.

<sup>2</sup> *Ann. Chem.* (Liebig), 269, 72.

<sup>3</sup> *J. Chem. Soc.* 1884, 587.

<sup>4</sup> *Loc. cit.*

nite information may be gained upon this interesting subject, although serious difficulties would be encountered in attempting to reach an altitude so high as to render the results of chemical tests positively conclusive.

WESTERN UNIVERSITY LABORATORY,  
ALLEGANY, PA.

### A NEW GENERATOR.

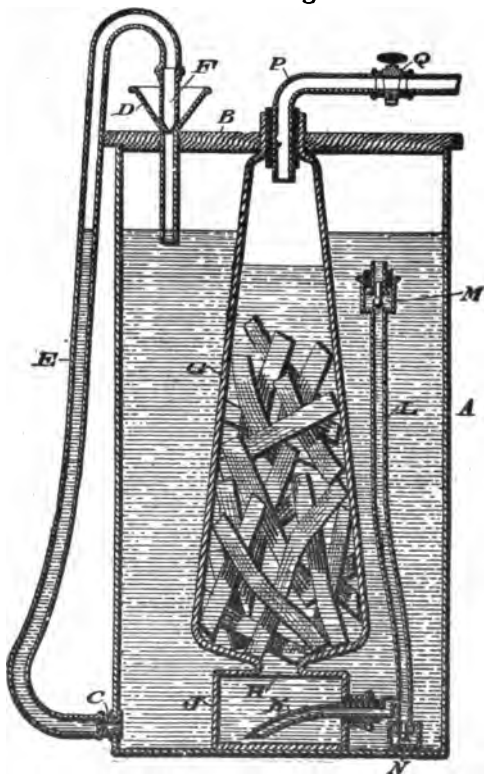
BY EDWARD P. HARRIS.

Received May 27, 1895.

A GREAT many forms of automatic generators for the preparation of such gases as hydrogen, hydrogen sulphide, carbon dioxide, etc., have been proposed, that known as the "Kipp apparatus" being probably most widely used.

The chief objection to this and other forms in general use lies in the fact that according to their construction the spent acid at the bottom of the reservoir, containing the metallic salts, is used over and over again until it becomes too weak for further action, while plenty of fresh acid remains in the upper part of the reservoir, unable to enter the inner chamber containing the solid material (zinc, iron sulphide, marble, etc.)

The accompanying figures show how this difficulty is removed by a very simple device. The second figure shows the side

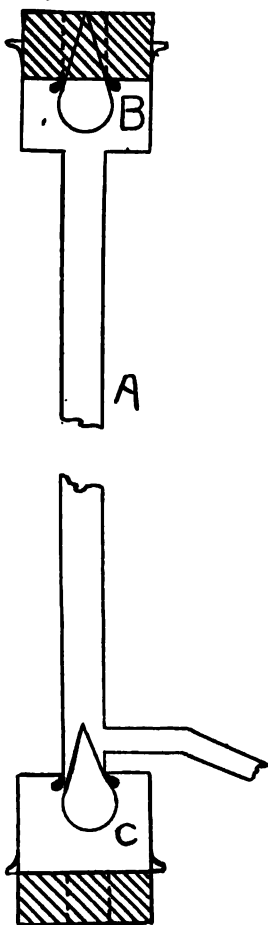


tube A enlarged. By mistake the artist has placed the side tube on the wrong side.

The bottom of the inner cylinder is closed and the flow of acid must be through the side tube A. This tube is connected with the lower part of the inner cylinder and is entirely immersed in the acid of the reservoir. At each end is a floating glass valve playing upon a rubber cushion at the end of the tube. When the gas is turned on and the pressure relieved from the inner cylinder the acid can enter only at B, and when the action is reversed the acid can escape only at C.

Thus, fresh acid from the upper part of the reservoir is always used and the spent acid containing the metallic salts is always deposited at the bottom where it remains, owing to its greater specific gravity. Once set up and charged the only attention this generator needs is the occasional withdrawal of some of the spent acid from the bottom and the addition of an equal quantity of fresh acid through the funnel at the top.

A generator of this description two and a half feet in height has furnished hydrogen sulphide for a class of thirty students in qualitative analysis for eight months, the only attention required being to fill the reservoir three times with acid. The apparatus may be obtained from Queen & Co. in three sizes. The largest size is particularly recommended for generating hydrogen sulphide.



CHEMICAL DEPARTMENT OF THE PENNSYLVANIA MILITARY COLLEGE,  
CHESTER, PA.



## THE DETERMINATION OF TANNIN BY METALLIC OXIDES.<sup>1</sup>

BY WILLIAM H. KRUG.

Received September 6, 1895.

THE following experiments were suggested by a method proposed for the estimation of tannin by Mr. Kerr, associate reporter on tannin, during the progress of the official work for the Association of Official Agricultural Chemists. This method consisted of the percolation of the tannin-bearing liquor through a column of asbestos with which a certain amount of yellow mercuric oxide had been intimately mixed. After making a number of attempts to obtain concordant results, I found it too difficult to secure uniform conditions such as rate of percolation, extent of contact and uniformity in the asbestos layer, and therefore turned to find some other way of using the oxide. It then occurred to me to substitute it for the hide-powder in the ordinary shaker method. During the work I extended the investigation to three other oxides, *viz.*, magnesium, zinc, and lead oxides.

At the beginning it was evident that much more time would be consumed in absorbing the tannin in this manner and a number of preliminary experiments were made to determine this time limit if possible. In all cases when, upon filtration after shaking a certain length of time, it was found that combination was incomplete, the solution was allowed to stand until this was accomplished. It was thus found, that with magnesium and mercuric oxides, it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration.

With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed. These two oxides were, therefore, rejected as requiring too much time, though the analyses made with them, are given below for comparison.

The extract used contained 42.35 per cent. soluble solids, and the diluted liquor used in the analyses, contained two grams of this extract per 100 cc. This diluted extract gave in twenty-

<sup>1</sup> Read at the Annual Meeting of the Association of Official Agricultural Chemists, Sept. 5, 1895.

five cc. as a mean of three determinations, 0.0113 gram ash, containing 0.0006 gram magnesium oxide.

The tannin was determined by the loss insolids, *i. e.*, twenty-five cc. of the filtrate were evaporated on the steam-bath in a weighed dish, dried three hours in a water-bath, and the weight of the residue determined. The difference between this weight and the solids in twenty-five cc. of the original diluted extract, was taken as tannins. The ash determinations were made as a check on the amount of the oxide dissolved during the analysis.

Experiments with zinc oxide.

Method.	Grams ZnO used.	cc. di luted extract used.	cc. of filtrate evaporated.	Weight of residue.	Per cent. of tannin in extract.	Grams ash in residue.	Grams ZnO in ash.
Shaken 4 hours, stood over night...2.0	75	25	0.1095	20.45	0.0125	0.0008	
" 4 " " " " ...2.0	75	25	0.1174	18.87	0.0147	0.0019	
Shaken 4 hours, stood one week...2.0	75	25	0.1049	21.37	0.0095	....	
" 4 " " " " ....2.0	75	25	0.1029	21.97	0.0103	0.0030	
" 4 " " " " ....2.0	75	25	0.1029	21.97	0.0100	0.0020	

The first two of these analyses gave a faint reaction for tannin, but were run through so as to compare the result with those obtained with other oxides. The low figures indicate incomplete combination. The last three gave no test for tannin when filtered, and agree fairly well. They are low, compared with lead and mercury oxides, and agree better with the results obtained with magnesium oxide. The amount of zinc oxide dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxide is the slow action. The last three analyses were tested every day for a week, before it was found that all the tannin had been absorbed. For this reason zinc oxide would be of no value in a laboratory where the rapid estimation of tannin is desired.

Experiments with lead oxide.

Method.	Grams PbO used.	cc. di- luted extract used.	cc. of filtrate evapo- rated.	Weight of residue.	Per cent. tannin in extract.	Weight of ash from residue.	Grams PbO in ash.
Shaken 3½ hours, stood 2 days...4.0	75	25	0.0738	27.59	0.0111	0	
" 3½ " " 2 " ...4.0	75	25	0.0754	27.27	0.0092	0	
" 3½ " " 2 " ...4.0	75	25	0.0706	28.23	0.0105	0	

None of these gave a reaction for tannin with ferric chloride. The results were higher than with any other oxide used. The objection to lead oxide is the length of time required for complete combination.

## Experiments with magnesium oxide.

Method.	Grams MgO used.	cc. di- luted extract used.	cc. filtrate evapo- rated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in resi- due.	Weight MgO in ash.
Shaken 2½ hours, stood over night...2.0	75	25		0.1134	19.67	0.0209	0.0055
" 2½ " " " " " ...2.0	75	25		0.1028	21.79	0.0195	0.0042
" 2½ " " " " " " ...2.0	75	25		0.1230	17.75	0.0232	0.0052
" 2½ " " " " " " ...2.0	75	25		0.1246	17.43	0.0247	0.0058
Stood 24 hours with occasional sh'k'g 2.0	75	50		0.2063	21.72	0.0252	0.0074
" 24 " " " " " " 2.0	75	50		0.2061	21.74	0.0244	0.0076
" 24 " " " " " " 2.0	75	25		0.1157	19.21	0.0213	0.0044
" 24 " " " " " " 2.0	75	25		0.1114	20.07	0.0205	0.0038
" 48 " " " " " " 2.0	75	50		0.1941	22.94	0.0326	0.0064
" 48 " " " " " " 2.0	75	50		0.1959	22.76	0.0339	0.0070
Shaken 3½ hours, stood over night...2.0	75	50		0.2165	20.70	0.0349	0.0102
" 3½ " " " " " " ...2.0	75	50		0.2191	20.44	0.0355	0.0111
" 3½ " " " " " " ...2.0	75	50		0.2179	20.56	0.0359	0.0115

This table shows that a considerable amount of the oxide is dissolved, and passes into the filtrate, increasing the weight of the residue, and correspondingly lowering the tannin. That this error may be quite considerable is shown by the fact that in almost every estimation, the ash is almost double that found in the original diluted extract. Furthermore, this error does not seem to be constant, so that no correction can be made for it.

## Experiments with mercuric oxide (yellow).

Method.	Grams HgO used.	cc. di- luted extract used.	cc. filtrate evapo- rated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in HgO in residue.	Weight ash.
Stood 48 hours with occasional sh'k'g 4.0	75	25		0.0833	25.69	0.0070	0
" 48 " " " " " " 4.0	75	25		0.0829	25.77	0.0077	0
" 48 " " " " " " 4.0	75	25		0.0829	25.77	0.0071	0
Shaken 1½ hours, stood over night...4.0	75	25		0.0842	25.51	.....	..
" 2 " " " " " " ...4.0	75	25		0.0867	25.01	.....	..
" 3½ " " " " " " ...4.0	75	25		0.0863	25.09	0.0081	0
" 3½ " " " " " " ...4.0	75	25		0.0860	25.15	0.0080	0
" 4 " " " " " " ...4.0	75	25		0.0839	25.57	0.0084	0
" 4 " " " " " " ...4.0	75	25		0.0849	25.37	0.0065	0
" 4 " " " " " " ...4.0	75	20		0.0638	26.41	0.0065	0
" 4 " " " " " " ...4.0	75	20		0.0692	25.05	0.0103	0
" 4 " " " " " " ...4.0	75	20		0.0682	25.29	0.0094	0
" 4 " " " " " " ...4.0	75	25		0.0863	25.09	0.0083	0
" 4 " " " " " " ...4.0	75	25		0.0849	25.37	0.0097	0
" 4 " " " " " " ...4.0	75	25		0.0842	25.51	0.0084	0

The above analyses show that even though the conditions may be varied, fairly concordant results can be obtained with mercuric oxide as long as care is taken to ensure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed, since, when it is reached, the yellow oxide

no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tannin-extract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

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### THE ESTIMATION OF SULPHUR IN REFINED COPPER.<sup>1</sup>

BY G. L. HEATH.

Received September 9, 1905.

SEVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius<sup>1</sup> proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hampe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

<sup>1</sup> Read at the Springfield Meeting.

<sup>2</sup> *Ztschr. anal. Chem.*, 13, 223.

very accurate one, for there are two or three possible sources of error.

1. The existence of the sulphur in different forms.
2. The incomplete removal of all oxygen and other impurities, from the chlorine gas.
3. The occasional formation of a layer of melted chloride, which may prevent the complete evolution of sulphur and combustion of copper.

A third method involves the use of potassium permanganate.

A fourth, and apparently, the most direct and satisfactory one, consists in dissolving ten grams of copper in nitric acid, or in a mixture of nitric with a little hydrochloric acid, and then precipitating the sulphuric acid directly from a hydrochloric acid solution, after removing all the nitric acid by repeated evaporation.

Upon this principle depends the method of H. J. Phillips.<sup>1</sup>

But the writer has repeatedly attempted to test refined copper by the last method, without obtaining any precipitate of barium salt. There should have been at least a trace of precipitate due to sulphur in the chemical reagents.

Though no refining on the large scale has ever produced metal in which a chemist could not find a trace of impurity, yet the best American refined copper of to-day, contains such a minute amount of sulphur, that a very delicate and accurate method is required for its estimation.

In order to test the influence of copper chloride and free hydrochloric acid upon barium sulphate, some experiments were made with solutions of pure copper chloride, and sulphuric acid.

It is a well known fact that certain substances interfere with the precipitation by barium chloride, and that barium sulphate is somewhat soluble in certain acids, and in solutions of copper.

The work of R. Fresenius,<sup>2</sup> F. W. Mar,<sup>4</sup> and others, has indicated that an excess of hydrochloric acid promotes the complete separation of barium sulphate, a conclusion rather contrary to earlier opinions.

<sup>1</sup> *Chem. News*, 6a, and *J. Anal. Appl. Chem.*, 5, 53.

<sup>2</sup> *Ztschr. anal. Chem.*, 9, 52 and 6a, also *Fres. Quant. Anal.*, Am. Ed. p. 139.

<sup>3</sup> *Am. J. Sci.*, 41, April 1891, also *J. Anal. Appl. Chem.*, 5, 278.

Mr. Mar states, as the writer has also noted, that the precipitation of minute quantities of barium sulphate is very much slower than that of large amounts.

Since the barium sulphate is not absolutely insoluble in water or dilute acid, the amount which would remain dissolved by a large volume of solution is appreciable, and cupric chloride may considerably influence the solubility.

As far as the time permitted, the experiments were carried out in two series; those analyses marked *a*, containing but a few drops of free hydrochloric acid, and those marked *b*, *c*, or *d*, about three and a half per cent. by volume of the same acid of 1.20 sp. gr.

Stock solutions were prepared as follows:

- a*. Standard sulphuric acid—1 cc.=0.00245 gram  $\text{BaSO}_4$ .
- b*. Cupric chloride solution—100 cc.=10 grams copper.

The solution used for all the experiments (except Nos. 12 *c*. and 12 *d*) was made by dissolving 100 grams of a very pure refined copper in 400 cc. of pure nitric acid, (sp. gr. 1.42), then precipitating the silver with a few drops of hydrochloric acid and filtering it off. The solution was then evaporated to dryness, and the evaporation repeated four times, with the addition of hydrochloric acid each time. The heat was continued until the chloride melted. The salt finally dissolved in water to a clear, faintly acid solution, which was diluted to one liter.

The slight trace of sulphur in the copper, was not any more than that found in the chemical reagents.

Ten grams of the copper yielded, by the author's method, only 0.0017 gram of barium sulphate, and the acids required for solution, gave 0.003 gram, for which allowance was made in the table of results.

*c*. As a check, some of the same copper was deposited by electrolysis from a nitric acid solution, and the pure plate was then redissolved, and after further treatment, the solution was used for experiments 12 *c* and 12 *d*, in which one cc. standard sulphuric acid was added to the diluted copper solution.

The measured portions of copper salt, water and acid were placed in beakers and the standard sulphuric acid run in from a

burette. The liquids were heated to boiling, treated with two to five cc. of a saturated solution of barium chloride, stirred, and allowed to stand at the temperature of the room for the number of hours specified in the table.

The precipitates of the tests marked (*b*, *c*, *d*,) were washed first with five cc. of dilute hydrochloric acid, (one part acid to twenty of water) and then with hot water. The ones marked (*a*) were washed with hot water only, and in two or three cases, a trace of copper was not washed out. (See experiments 11*a*, and 15*a*).

At least a few drops of dilute acid should be always used in the first washing by decantation.

The results are tabulated according to the degree of dilution, and the weight of copper in the solution.

TABLE I.

ONE-TENTH GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS SEVENTY CC.

Faintly acid two-tenths free hydrochloric acid.					Strongly acid two and a half cc. hydrochloric acid added.				
		Gram barium sulphate.					Gram barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
1 <i>a</i>	24	0.0025	0.0027	+0.0002	1 <i>b</i>	24	0.0025	0.0027	+0.0002
2 <i>a</i>	24	0.0123	0.0127	+0.0004	2 <i>b</i>	24	0.01235	0.0124	0.0000
3 <i>a</i>	24	0.04905	0.0489	—0.00015	3 <i>b</i>	24	0.0491	0.0497	+0.0006

TABLE II.

ONE GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS, 350 CC.

Slightly acid two-tenths cc hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid.				
Time in		Gram barium sulphate.		Difference	Time in		Gram barium sulphate.		Difference.
No.	hours.	Taken.	Found.		No.	hours.	Taken.	Found.	
4 <i>a</i>	24	0.0029	0.0026	—0.0003	4 <i>b</i>	24	0.0029	0.0009	—0.0020
5 <i>a</i>	24	0.0126	0.0115	—0.0011	5 <i>b</i>	24	0.0126	0.0101	—0.0025
6 <i>a</i>	24	0.0495	0.0446	—0.0049	6 <i>b</i>	34	0.0495	0.0385	—0.0110
6 <i>a</i>	72	0.0495	0.0490	—0.0005	6 <i>b</i>	72	0.0495	0.0493	—0.0002
7 <i>a</i>	72	0.2455	0.2445	—0.0010	7 <i>b</i>	72	0.2462	0.2500	+0.0038

TABLE III.

TWO AND A HALF GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 350 CC.

Slightly acid two-tenths cc. hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid added.				
No.	Time in hours.	Gram of barium sulphate. Taken.	Found.	Difference.	No.	Time in hours.	Gram of barium sulphate. Taken.	Found.	Difference.
							0.0046	0.0000	-0.0036
8a	24	0.0036	0.0007	-0.0029	8b	24	0.0936	0.0006	-0.0030
					8c	72	0.0036	0.0014	-0.0022
9a	72	0.0135	0.0129	-0.0006	9b	72	0.0135	0.0128	-0.0007
					9c	140	0.0145	0.0131	-0.0014
10a	72	0.0502	0.0496	-0.0006	10b	24	0.0502	0.0493	-0.0009
					10c	72	0.0502	0.0492	-0.0010
					10d	140	0.0502	0.0501	-0.0001
11a	72	0.2470	0.2505?	+0.0035	11b	72	0.2470	0.2486	+0.0016

TABLE IV.

TEN GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 700 CC.

Faintly acid one-half cc. hydrochloric acid.					Strongly acid twenty-five cc. hydrochloric acid added.				
No.	Time in hours.	Gram barium sulphate. Taken.	Found.	Difference.	No.	Time in hours.	Gram barium sulphate. Taken.	Found.	Difference.
		0.0074	0.0000	-0.0074					
12a	24	0.0074	0.0000	-0.0074	12b	24	0.0074	0.0000	-0.0074
					{ 12c 140 12d "		0.0057	0.0005	-0.0052
							0.0057	0.0004	-0.0053
13a	72	0.0170	0.0102	-0.0018			0.0165	0.0014	-0.0151
					13b	24	0.0165	0.0013	-0.0153
14a	lost				13c	72	0.0165	0.0051	-0.0114
					14b	24	0.0540	0.0502	-0.0038
					14c		0.0540	0.0400	-0.0140
15a	72	0.2509	0.2551?	+0.0047	15b	24	0.2500	0.2389	-0.0111
						72	0.2500	0.2436	-0.0064
						140	0.2500	0.2474	-0.0026

The results, given in Table I., show that if the total volume of a solution is not over 100 cc. the barium sulphate is completely precipitated, whether the liquid is strongly acidified or not.

Table II: If the volume of the solution is increased to 350 cc. and the copper to two and a half grams, the precipitation is complete, even then, under the given conditions, in 72 hours with the exception of the analysis containing but a trace of sulphuric acid.



Tables III and IV : In the presence of as much as ten grams of copper in solution, the deposition becomes very slow indeed, as the results prove, and the strongly acidified solutions, at least retain appreciable amounts of barium sulphate.

Since the solubility of barium sulphate varies according to the conditions somewhat, the figures given by Fresenius, F. W. Mar, and others would not express the true effect of the water and dilute hydrochloric acid if the conditions of acidity, temperature, dilution, etc., were not the same. So a few experiments were made to determine the solvent effect of the water and acid alone.

Analyses 16-20 indicate that a part at least of the deficiency noted in the other tables is due to the solubility of the precipitate in the large volume (700 cc.) of dilute acid.

TABLE V.

No.	cc. of hydrochloric acid.	Temperature during settling.	Total volume.	Time in hours.	Gram barium sulphate.		
					Taken.	Found.	Difference.
16	25	20° C.	700	48	0.0025	0.0008	-0.0017
17	25	20° C.	700	48	0.0123	0.0086	-0.0037
18	25	20° C.	700	48	0.0490	0.0470	-0.0020
19	2 cc. + 5 grams ammonium chloride.		70	3	0.0490	0.0487	-0.0003

Fresenius<sup>1</sup> states that 1,000 parts of cold hydrochloric acid containing 3 per cent. dissolve 0.06 parts BaSO<sub>4</sub>.

Other experiments proved, however, that if a solution be kept at a temperature above 75° C., after the addition of barium chloride, the separation of barium sulphate is far more rapid and complete.

Cupric chloride appears to retard the deposition, especially when strongly acidified.

Direct precipitation in a moderately acid solution of this salt is determined to be sufficiently accurate for mattes and crude copper, but the separation of minute amounts of barium sulphate, from a very large volume of chloride solution, is too uncertain to permit the use of such a method for the detection and estimation of traces of sulphur in the best modern refined copper.

<sup>1</sup> F. Quant. Anal., 1st Am. Ed., p. 139, from Anal. Chem., 9, 62.

In 1889 the late Dr. L. M. Norton and the author of this paper devised and adopted a simple method, which has been improved by the latter, and has given very accurate results.

The complete precipitation of the barium sulphate is made possible in every case by first removing the copper electrolytically and then treating the solution as in the following scheme:

Take for analysis sufficient copper to yield a weighable amount of barium sulphate—ten grams will usually be enough.

Dissolve in a large beaker, placed over an alcohol flame, by means of a mixture of 60 cc. nitric acid (1.42 sp. gr.) and 15 cc. of hydrochloric acid (1.20 sp. gr.).

When dissolved, raise the lamp wick and evaporate nearly to dryness, then evaporate again after adding 50 cc. strong nitric acid.

Repeat this operation with another portion of the same acid, then redissolve in 300 cc. of water, and add a little nitric acid if a trace of basic salt remains undissolved.

The addition of hydrochloric acid and the consequent evaporation with nitric may be dispensed with, if experiment shows that nitric acid alone will oxidize all the sulphur in the class of material operated upon.

Next, pour the liquid through a small filter into a 700 cc. beaker and dilute with distilled water to 600 cc. or more.

Introduce as a negative electrode a large cone, or as is more convenient, a sheet of platinum, 4 by 5 inches.

Any wire or small piece of platinum foil will serve as a positive electrode.

Cover the beaker with glass and connect the electrode, preferably with an Edison incandescent lamp circuit.

The current from two sixteen candle-power lamps, coupled in parallel, will deposit the copper in one night.

When the liquid is colorless, or nearly so, remove the electrodes and wash them with distilled water, allowing the water to run into the main solution.

Pour off the liquid, if clear, from any bits of spongy copper, washing these on a small filter.

In order to prevent the escape of any sulphuric acid during subsequent evaporation, add, at this point, one-tenth gram dry,

pure sodium carbonate, (or a half gram for crude copper).

Evaporate the solution to dryness, as rapidly as possible without loss, in a No. 3 or No. 4, porcelain casserole. An alcohol lamp should be used, and the dish protected from dust. The evaporation may be completed on the water-bath, but if the dish is covered near the end of the operation and the flame regulated, there need be no loss by spattering, though the liquid be taken to dryness over the lamp. As soon as the salts in the dish are dry, heat the covered casserole quite strongly, with the lamp held in the hand, until the acid ammonium nitrate suddenly volatilizes, and then allow it to cool.

At this point is the only danger of loss of sulphur, and the heat should be just high enough to volatilize the nitrate. This heating may possibly be omitted if there is but a trace of ammonium nitrate in the dish. (See experiment 19).

Add to the residue, ten cc. strong hydrochloric acid and five cc. water, and evaporate to dryness on the water-bath. Repeat the process and then add one cc. of strong hydrochloric acid, add fifty cc. of water and dissolve, filter into a small beaker and wash the filter with hot water.

If the copper is known to be high in sulphur, the solution may be diluted to 150 cc. or more.

The only impurity of copper which might interfere with this method is lead. If lead is present, it will mostly remain in solution and be deposited on the plate, but if any lead sulphate remains on any of the filters, they must be boiled with a little solution of pure sodium carbonate, the solution filtered, and the sulphuric acid recovered from the acidified liquids as barium sulphate.

Heat the solution of sodium sulphate to boiling, precipitate with a slight excess of barium chloride, and allow the precipitate to settle twenty-four hours, unless the results are desired at once, in which case the precipitation may be completed inside of three hours, by keeping the liquid at a temperature not less than 75° C. during that time.

The acids and distilled water, used in the analysis, should be measured, and a blank analysis carefully made by evaporating with the pure soda, and the trace of barium sulphate deducted

from that of the analysis proper. Exp. 20-22 are three comparative analyses from the writer's note-book.

TABLE VI.  
COPPER ANALYSIS.

		Per cent. sulphur.			Per cent. sulphur.
20	Direct precipitation	0.0000		Author's method	0.0023
21	" "	0.6000		" "	0.6500
22	" "	0 to 0.0050		" "	(1) 0.0112
22	Chlorine method	0.0189?		" "	(2) 0.0094

It is evident that the method just detailed, is extremely well adapted to the analysis of refined copper.

The sulphur in the metal is brought into solution, and finally precipitated in a pure condition without loss, and a blank analysis is possible under the same conditions. The difference between the two results, expresses the true quantity of sulphur present.

Another chemist stated sometime ago that he, also, had been obliged to try a similar plan. The author has, however, worked out the foregoing process in its improved form independently, and in presenting this standard method, desires to express his indebtedness to the gentleman who has so kindly consented to read the paper before the assembly.

## ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.<sup>1</sup>

BY LYMAN F. KEBLER.

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THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behavior with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schlössing<sup>2</sup> proposed the method and applied it to the titration of nicotine with a view of establishing its equivalent; using sulphuric acid and litmus in his work. Sixteen

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> 1847, *Comp. rend.*, 23, 1142; 1847, *Ann. Chim. Phys.* [3], 19, 230; *Chem. Gaz.*, 5, 41; *Am. J. Pharm.*, 19, 68.

years later the work was taken up by Wittstein,<sup>1</sup> who was followed by F. M. Brandl,<sup>2</sup> Liecke,<sup>3</sup> Kosutany,<sup>4</sup> and G. Dragendorff.<sup>5</sup> Up to this time nicotine and conine were the only alkaloids operated on, and litmus the only indicator employed. In 1879 L. van Itallie<sup>6</sup> extended the work to several other alkaloids, using lacmööid as indicator. A. W. Gerrard<sup>7</sup> a few years later employed litmus and phenolphthalein in titrating the alkaloids of belladonna. From the contributions of O. Schweissinger,<sup>8</sup> who used cochineal as indicator, and those of E. Dieterich<sup>9</sup> and P. C. Plugge<sup>10</sup> we may ascribe the impetus which the titration of alkaloids with volumetric acid solutions received at the beginning of the present decade.

The method had been gaining ground rapidly when several most valuable communications appeared by C. C. Keller,<sup>11</sup> of Zürich, since which great improvement has been made.

In volumetric analysis, the first question demanding attention is a suitable indicator or delicate end reaction.<sup>12</sup> The object of this communication is to present the results of a study of five indicators in titrating alkaloids, thinking perhaps it may be of some service in formulating systematized methods of analysis in alkaloidal chemistry. The discordant results of analysis often obtained by different chemists operating on the same sample are greatly to be regretted. It is the writer's opinion that

<sup>1</sup> 1862, *Vierjahrsschr. prakt. Pharm.*, 11, 351.

<sup>2</sup> 1864, *Vierjahrsschr. prakt. Pharm.*, 13, 322.

<sup>3</sup> 1865, *Mittheilungen des hannov. Gew.-Ver.*, p. 160; *Ding. poly. J.*, 178, 235; *Polyt. Notizbl.*, No. 20; *Ztschr. anal. Chem.*, 4, 492.

<sup>4</sup> 1873, Kosutany, *Anal. Bestim. einiger Bestandth. d. Tabakspflanze*. Diss. Altenburg, Hungary.

<sup>5</sup> 1874, *Chem. Werthbestim.*, p. 42 and 55; see also *Plant Analyses*, 1884, Eng. Ed., pages 63 and 188.

<sup>6</sup> 1879, *Nederland. Tydschr. v. Pharm.*, Jan; *Analyst*, 14, 118.

<sup>7</sup> 1882 and 1884, *Year-Book of Pharm.*, p. 401, 447.

<sup>8</sup> 1886, *Pharm. Centralhalle*, 27, 492.

<sup>9</sup> 1887, *Pharm. Centralhalle*, 28, 21; *Pharm. J. Trans.* [3], 17, 888; *Am. J. Pharm.*, 59, 179.

<sup>10</sup> 1887, *Arch. d. Pharm.* [3], 25, 45, 49; *J. de Pharm. et de Chim.* [5], 15, 571; *Ber. d. chem. Ges.*, 20, 148; *J. Chem. Soc.*, 52, 621.

<sup>11</sup> 1892, *Schweiz., Wochenschr. f. Chem. u. Pharm.*, 30, 501, 509; *Am. J. Pharm.*, 65, 78. 1883, *Schweiz., Wochenschr. f. Chem. u. Pharm.*, 31, 473; *Ztschr. Oesterreich-Apoteker.*, 47, 563, 586; *Am. J. Pharm.*, 66, 42.

<sup>12</sup> Alkaloids, generally, are neutral to phenolphthalein, consequently it cannot be employed in titrating alkaloids directly. It is available for indirect titrations, i. e., estimating the amount of acids combined with an alkaloid in its neutral salts.

the discrepancies are chiefly due to differences in *modus operandi*, to defective apparatus, and, in volumetric analysis, to different end reaction tints arbitrarily assumed by each worker.

In order to eliminate the factors of uncertainty as completely as possible the methods of operation were carefully written out and closely adhered to in all the work. The burettes and a pipette were carefully calibrated in order to ascertain the necessary factor for correction. The method of calibration was as follows: each burette and pipette was exactly filled to the zero mark with distilled water, at 15° C. and ten cc., delivered into a tared weighing flask and weighed, then the next ten cc. were treated in the same manner, and so on until the entire capacity of each was tested. A glass-stoppered cylinder was also standardized. All efforts to standardize a liter flask were thwarted. A large balance sufficiently sensitive to do the work satisfactorily could not be found.

In titration the personal equation plays an important part. Authorities are not agreed on end reaction tints, each operator relying on his own judgment. The writer thinks it correct to titrate to the point where a different color from the initial color is developed. In order to obtain standard end reaction tints for alkaloids it will be necessary to prepare some absolutely pure alkaloid; treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid color reaction. For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared.

In this work the writer titrated from acid to alkaline solutions as follows: Brazil wood, from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish-red; haematoxylin from yellow to brown-orange; litmus from red to onion-red, and methyl orange from red to straw-yellow.

The indicator solutions were prepared according to the most approved processes. Cochineal and litmus were prepared according to the specifications of Sutton's Volumetric Analysis, sixth edition. Phenolphthalein, one gram dissolved in one liter of fifty per cent. alcohol. Haematoxylin, well crystallized, one

gram dissolved in 100 cc. of strong alcohol. The method best suited for preparing the Brazil wood solution, is to place three grams of the wood into a casserole, add ten cc. of distilled water, boil gently for a few minutes, cool, and filter. A freshly prepared solution has given the writer the most satisfactory results. Methyl orange, one gram dissolved in one liter of distilled water. Considerable difficulty was experienced in obtaining even a fairly satisfactory product of methyl orange. The method proposed by Mr. B. Reinitzer<sup>1</sup> for preparing the litmus solution did not come to the writer's notice until considerable work had been done with the solution prepared as above.

In titration the following quantities of the several indicators were employed: methyl orange, Brazil wood, cochineal, and phenolphthalein, five drops each; litmus ten drops and haematoxylin three drops.

The standard solution employed in this investigation, from which the exact strength of the other volumetric solution was determined, was a solution of normal sulphuric acid. This solution was prepared from data obtained by the several methods; titration against pure anhydrous sodium carbonate, using the above indicators; precipitation as barium sulphate and Weinig's<sup>2</sup> process. After some experimentation, it was found that Weinig's method gave the most satisfactory results. The method is simple and yields very concordant results. The following are the data obtained from an approximately normal sulphuric acid solution with the above methods:

Indicators. and methods.	No. of cc. of acid solution required per ten cc. of normal sodium carbonate.	Grams of SO <sub>3</sub> in ten cc. of the acid solution.
Brazil wood.....	9.50	0.4211
Haematoxylin .....	9.54	0.4192
Cochineal.....	9.50	0.4211
Litmus .....	9.50	0.4211
Methyl orange.....	9.50	0.4211
Phenolphthalein.....	9.45	0.4216
Weinig's method .....	....	0.4247
Barium sulphate method..	....	0.4200

Due precaution was taken to boil the solution thoroughly with

<sup>1</sup> 1894, *Ztschr. angew. Chem.*, 547, 573; *Chem. News*, 70, 225, 239, 249.

<sup>2</sup> 1892, *Ztschr. angew. Chem.*, 204; *Analyst*, 17, 99.

the indicators requiring it. With solutions of the above strength it was impossible to detect any difference in the sensitiveness of most of the indicators.

With the normal sulphuric acid solution a normal solution of pure potassium hydroxide was standardized. From the normal sulphuric acid solution and normal alkaline solution there were prepared, respectively, a decinormal acid solution and a centinormal alkaline solution. The two solutions thus prepared were carefully titrated against each other, employing the above indicators with the following results :

Indicators.	No. of cc. of normal sulphuric acid.	No. of cc. of centinormal KOH required per ten cc. of deci- normal $H_2SO_4$ .	
		LaWall.	Kebler.
Phenolphthalein.....	10	101.80	102.00
Brazil wood.....	10	99.56	100.00
Cochineal.....	10	100.58	99.80
Haematoxylin .....	10	99.76	100.00
Litmus .....	10	99.97	99.60
Methyl orange .....	10	92.67	98.53

My associate, Mr. LaWall, took up a portion of the work, which he executed independently, using, however, the same solutions and apparatus that the writer employed. The above, and all subsequent results, are the average of duplicate, triplicate or more titrations.

The titration of pure alkaloids, as found in the market, was next undertaken. With quinine and codeine the following method was used: two grams of the alkaloid were placed in the cylinder, dissolved in alcohol, and diluted up to 100 cc. with alcohol. To ten cc. of this solution and the requisite quantity of indicator contained in a suitable beaker, the decinormal acid solution was added to slight excess, agitated, allowed to stand a few minutes, the sides of the beaker well washed down with distilled water, adding about forty cc., and the excess of acid titrated back with the centinormal alkaline solution.

With alkaloids not freely soluble in alcohol, the following procedure was adopted: two grams of the alkaloid were placed into a 200 cc. beaker, seventy-five cc. of decinormal acid added, the contents of the beaker warmed on a water-bath and occasionally agitated until the alkaloid was dissolved. The beaker



and contents were then cooled, the contents transferred to a 100 cc. cylinder, the beaker carefully rinsed with several successive portions of water, transferred to the 100 cc. cylinder and finally made up to 100 cc. with water. Each ten cc. contained two-tenths of a gram of alkaloid and seven and a half cc. of decinormal acid solution. After adding the requisite amount of indicator to ten cc. of the alkaloidal solution and diluting up to about fifty cc., the excess of acid was carefully retitrated. Two or more titrations were made in every case, with the same solution and indicator, by adding to the solution just finished, another portion of the decinormal acid solution and retitrating with the centinormal alkaline solution, taking finally the average reading.

The above methods of titration and preparation of solutions were employed with several pure alkaloids. The results are tabulated below.

Indicators.	Quinine.		Strychnine.		Morphine.	Codeine.
	La Wall.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.
Brazil wood.....	99.90	101.97	99.36	98.93	95.75	
Cochineal .....	105.56	102.54	103.20	99.08	97.09	
Haematoxylin .....	99.81	103.37	100.03	98.17	95.90	
Litmus .....	101.80	103.55	103.54	98.93	96.38	
Methyl orange.....	....	123.27	104.21	100.59	98.11	

The number of times the analyst is requested to investigate the purity of refined alkaloids is comparatively small, but the crude alkaloids claim a greater share of his time and attention.

The next step was to investigate the adaptability of the above process to crude morphine and crude cocaine. The results are as follows :

Indicators.	Crude morphine.		Crude cocaine.
	La Wall.	Kebler.	Kebler.
Brazil wood.....	99.23	98.47	95.90
Cochineal.....	100.14	99.53	97.11
Haematoxylin .....	99.08	97.59	95.74
Litmus .....	99.50	98.93	96.82
Methyl orange.....	102.10	100.02	100.14

With the same crude morphine the ash method yielded 97.59 per cent., the lime-water method 98.22 per cent., and the absolute alcohol method 98.33 per cent. of pure morphine.

A complete analysis was made of the crude cocaine to ascer-

tain how nearly the titrations corresponded with the gravimetric process of Dr. Squibb.<sup>1</sup>

	Per cent.
Moisture .....	0.405
Cocaine nearly pure .....	97.300
Material soluble in ether .....	0.100
Material insoluble in ether .....	1.810
Loss .....	0.385
Total.....	100.00

Notwithstanding the fact that crude alkaloids claim considerable attention on the part of the analyst, yet only a few are found already extracted on the market. It generally happens that the operator is requested not only to determine the amount of pure alkaloids, but also to extract them from their natural sources. For this purpose the writer employed a modification of Keller's process. The method is as follows: place ten grams of the dry drug into a 250 cc. flask, add twenty-five grams of chloroform, seventy-five grams of ether, stopper the flask securely, agitate well for several minutes, add ten grams of ten per cent. ammonia water, then agitate frequently and during one hour. On adding five grams more of ten per cent. ammonia water and shaking well, the suspended powder agglutinates into a lump, the liquid becomes clear, after standing a few minutes, and can be poured off almost completely.

1. When the mixture has completely separated, pour off fifty grams into a beaker, evaporate the solvent on a water-bath, add ten cc. of ether, and evaporate again. Dissolve the varnish-like residue in fifteen cc. of alcohol, with heat, add water to slight permanent turbidity, the requisite quantity of indicator and an excess of the acid solution; retitrate with the centinormal alkaline solution.

2. When the mixture has completely separated pour fifty grams into a separatory funnel, treat at once with twenty cc. of acidulated water. After thorough agitation and complete separation remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with fifteen cc. of slightly acidulated water. The acidulated water

<sup>1</sup> *Ephemeris*, 3, 1171.

in the second separatory funnel is rendered alkaline with ammonia water, the alkaloid removed successively with twenty cc., fifteen cc., and fifteen cc. of a mixture of three parts (by volume) of chloroform and one part of ether. Collect the chloroform-ether mixture in a tared beaker and distil off the solvent. The varnish-like residue is twice treated with eight cc. of ether, evaporated on a water-bath and dried to constant weight on the water-bath. The varnish-like residue is next dissolved in fifteen cc. of alcohol and treated as in (1) above.

Nux vomica and ipecac root were treated according to processes (1) and (2); belladonna leaves according to process (2). The results are as follows:

	Per cent. of alkaloids in nux vomica by process (1).		Per cent. of alkaloids in nux vomica by process (1). Gravimetrically.		Per cent. of alkaloids in nux vomica by process (2). Volumetrically.		Per cent. of alkaloid in ipecac root by process (1).	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood.....	2.04	2.58	2.94	3.00	2.37	2.37	2.46	2.54
Cochineal .....	2.64	2.69	2.86	3.10	2.42	2.39	2.59	2.49
Haematoxylin ...	2.18	2.24	2.88	3.11	2.23	2.27	2.48	2.54
Litmus .....	2.38	2.34	2.93	3.05	2.55	2.37	2.55	2.57
Methyl orange...	3.02	3.64	2.93	3.02	2.65	2.61	2.95	3.30

	Per cent. of alkaloid in ipecac root by process (2).		Per cent. of alkaloid in ipecac root by process (2). Gravimetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Gravimetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Volumetrically.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood.....	2.58	2.60	2.36	2.35	0.26	0.20	0.19	0.15
Cochineal .....	2.63	2.68	2.52	2.33	0.28	0.20	0.24	0.14
Haematoxylin ...	2.58	2.68	2.35	2.33	0.27	0.22	0.21	0.13
Litmus .....	2.62	2.60	2.40	2.25	0.24	0.18	0.20	0.15
Methyl orange...	2.66	2.63	2.89	2.61	0.25	0.20	0.23	0.20

According to the well-established method of Messrs. Dunstan<sup>1</sup> and Short, the nux vomica examined contained 2.89 per cent. of crude alkaloid. On carefully titrating this crude product with a volumetric acid solution, 2.12 per cent. of pure alkaloid was indicated. Cochineal was used as an indicator. These figures show that this method produces an alkaloid residue containing a smaller percentage of pure alkaloid than that obtained by Keller's process.

<sup>1</sup> 1883, Pharm. J. Trans. [3], 13, 665.

From the results embodied in this paper it can safely be concluded that methyl orange cannot be numbered with the indicators suitable for titrating alkaloids. With centinormal, fifth decinormal and other solutions of various strengths it fails to give satisfactory results. Notwithstanding the sensitiveness claimed for it, the writer believes that its days, as an ideal indicator, are numbered. Even Professor Lunge, the staunch advocate of methyl orange, has admitted that a properly prepared solution of litmus is quite superior to this indicator, in inorganic estimations.

A solution of litmus prepared according to the directions herein employed is quite unsatisfactory for delicate titrations. The method proposed by Reinitzer promises to be better suited.

Of the indicators thus far considered, haematoxylin, Brazil wood, and cochineal give very promising results. Haematoxylin justly claims first place and Brazil wood the second. Other indicators will be considered in due time.

As stated above, the prime object of this investigation is to ascertain what indicators are best adapted to the titration of alkaloids; but in order to determine how reliable the results were, gravimetric determinations necessarily formed a part of the work.

When it is remembered that not only do analytical methods contain inherent limitations, but also that each operator possesses a positive or a negative equation of error, the reader will undoubtedly concur with the writer that the results are very satisfactory. Attention must again be called to the fact that the work was conducted under precisely the same conditions.

As would naturally be expected, the amount of alkaloid obtained by process (2) is smaller than that secured by process (1). A small per cent. of the alkaloid may be lost during the process of extraction. The small amount of coloring-matter possibly vitiates the results, or perhaps some non-alkaloidal substance increases the yield in process (2).

From the hundreds of assays made by the author, he feels justified in stating that all of the gravimetric processes yield products containing considerable non-alkaloidal matter, and hopes that the day is not far distant when all gravimetric results

will at least be supplemented by volumetric methods, if not displaced by them.

THE MORE VALUABLE LITERATURE ON INDICATORS DURING THE LAST TWO DECADES.

1877. E. Luck: *Ztschr. anal. Chem.*, 16, 332.  
1880. A. Baeyer: *Ann. Chem. (Liebig)* 202, 68.  
1881. R. B. Warder: *Am. Chem. J.*, 3, 55.  
1882. G. Tobias: *Ber. d. chem. Ges.*, 15, 2452.  
1883. R. T. Thomson: *Proc. Phil. Soc., Glasgow*, 14, 56, 173; *Chem. News.*, 47, 123, 135, 184.  
1883. H. Beckurts: *Pharm. Centralhalle*, 24, 333; *Abstr., Ber. d. chem. Ges.*, 17, 3073.  
1883. J. Wieland: *Ber. d. chem. Ges.*, 16, 1989.  
1883. R. T. Thomson: *Proc. Phil. Soc. Glasgow*, 15, 63, 194; (1884) *Chem. News*, 49, 32, 38, and 119.  
1884. H. Beckurts: *Pharm. Centralhalle*, 25, 101; *Abstr., Ber. d. chem. Ges.*, 17, 238.  
1884. C. Kraemer: *Ber. d. chem. Ges.*, 17, 1875.  
1884. F. A. Flückiger: *Arch. d. Pharm.* [3], 22, 605.  
1885. G. Lunge: *Ber. d. chem. Ges.*, 18, 3290.  
1885. R. T. Thomson: *Chem. News*, 52, 18, 29.  
1885. M. Berthelot: *Comp. rend.*, 100, 207; *Abstr., Ber. d. chem. Ges.*, 18, 93.  
1885. M. C. Traub: *Arch. d. Pharm.* [3], 23, 27; *Abstr., Ber. d. chem. Ges.*, 18, 126.  
1885. M. Dechan: *Pharm. J. Trans.* [3], 15, 849.  
1885. J. H. Long: *Chem. News*, 51, 160.  
1885. H. N. Draper: *Chem. News*, 51, 206.  
1885. R. Engle and J. Ville: *Bull. Soc. Chim.*, 44, 17.  
1885. B. Fischer and O. Philipp: *Arch. d. Pharm.* [3], 23, 434; *Abstr., Ber. d. chem. Ges.*, 18, 583.  
1885. T. Lehmann and J. Petri: *Arch. d. Pharm.*, [3], 23, 243; *Abstr., Ber. d. chem. Ges.*, 18, 625.  
1889. J. H. Long: *Am. Chem. J.*, 11, 84.  
1891. A. H. Allen: *Analyst*, 17, 186, 215.  
1891. G. Lunge: *J. Soc. Chem. Ind.*, 10, 314.  
1891. J. Lüttke: *Apoth. Ztg.*, 7, 643; *Ztschr. anal. Chem.*, 31, 692.  
1893. M. B. Breed: *J. Frank. Inst.*, 135, 312; *J. Anal. Appl. Chem.*, 7, 204.  
1893. R. T. Thomson: *J. Soc. Chem. Ind.*, 12, 432.  
1894. B. Reinitzer: *Ztschr. angew. Chem.*, 547, 573; *Chem. News*, 70, 225, 239, 249.  
1894. G. Lunge: *Ztschr. angew. Chem.*, 733.  
1894. W. Schafer: *Apoth. Ztg.*, 9, 839; *Abstr., Analyst*, 20, 37 (1895).

## NEW BOOKS.

ELEMENTS OF MODERN CHEMISTRY. BY CHARLES ADOLPHE WURTZ. Fifth American Edition. Revised and enlarged by Wm. H. Greene, M.D., and Harry F. Keller, Ph.D. 12 mo. pp. 788. Philadelphia: J. B. Lippincott & Co., 1895.

On the whole, this is a very good text-book, well adapted to the needs of high schools and general use in colleges, as its popularity proves. From the reviewer's standpoint, however, it possesses two distinct faults. First, the disproportionately large space given to organic chemistry. This part of the subject is full of very important information, but it has taken on too much of the style of a dictionary and too little of the analytical method of a treatise. The result is 360 pages of material which by judicious generalization should have been condensed to half that amount, in order to correspond in size to the rest of the book. For instance, two pages are given to describing succinic acid, and yet barely a single page each to barium, strontium or cadmium, with all their compounds; the derivatives of urea take five pages, while the subject of chemical energy and thermochemistry is disposed of in just half that space. Secondly, the lack of true inductive reasoning in establishing the probability of the atomic theory. The introductory pages on chemical theories and laws contain the "Articles of Faith" of the atomic theory, very clearly stated, but it must be said that the theory itself is virtually taken for granted. For instance, speaking of forming ferrous sulphide by melting iron filings and sulphur together, it is said, "After cooling it is perfectly homogeneous, neither iron nor sulphur can be recognized. Both have disappeared as such." This is perfectly true, and according to experience. But, a few lines further we have: "It cannot be admitted that these two substances are confounded in the molecule, or that the effect of the combination of sulphur with iron is an interpenetration of the two bodies, so intimate that they both disappear in what might be called a homogeneous mixture." The student might very naturally inquire why it could not be admitted, since such an admission would coincide so well with the facts as far as we know them; and the only answer that

could be made would be, "It would not agree with the atomic theory." The student might well say, "So much the worse for the theory!"

We note the absence of thermochemical data, the most important of which might well serve for illustrating the general relations of the elements to each other and to the acids. In the chapters describing the metals and their compounds, many of the simple blowpipe tests for identifying the elements are omitted, and for some common elements no qualitative tests at all are given. The table of the melting-points of the metals needs revision. The electrolytic method of refining copper cannot now be spoken of as expensive. The mineral Edisonite, spoken of as a form of titanite oxide, has been proved to be rutile. Among the methods of manufacturing caustic soda, bleaching powder, and potassium chlorate, the electrolytic methods are not mentioned—as they surely should be.

On the other hand, the numerous revisions to which the text has been subjected have ensured the almost certain accuracy of the facts presented and the absence of mistakes. The revision up to date has been done in a way which reflects great credit on the revisers. Granted that the teacher will remedy the faults first spoken of by cutting down much of the detail of the organic chemistry and presenting the atomic theory in a more logical manner, and we may pronounce the book the best elementary text-book of chemistry of the year.

JOSEPH W. RICHARDS.

JUSTUS VON LIEBIG, HIS LIFE AND WORK. BY W. A. SHENSTONE. 12mo. pp. 219. \$1.25. New York: Macmillan & Co.

Liebig's personality was an interesting one. His life was one of earnest purpose and hard work. He was a many-sided man, and his influence was felt in many directions. In investigation, as a man of affairs and as a popular teacher, Liebig's work has been of use to his kind. Of the brilliant chemists of his day—Graham, Dalton, Wöhler and Dumas, among others—his career is the most interesting. Liebig's work began in Gay Lussac's laboratory where in connection with his work on the fulminates he discovered isomerism. In 1824 he went to Giessen, and in 1852 to Munich. "Liebig was essentially a pioneer in science.

In the course of his life he took the lead in no less than four great departures. The first was in organic chemistry, the second and third in the application of chemistry to agriculture and physiology, the fourth \* \* was the outcome of his labors as a teacher. His work, like that of other pioneers was, of course, not always correct in all points of detail. But it had all the greater merits of good pioneering work in a most marked degree. It almost always pointed the right way, and its remarkable influence in determining the direction of subsequent research has been singularly permanent." To this may be added that he was a virile man, vigorous and trenchant in debate, but honoring truth above all things, and willing to acknowledge his errors—and several times he was in the wrong.

Professor Shenstone has given us a very interesting and lucid account of his life and his work.

R. H.

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NOTE.

*Determination of Acetic Acid in Vinegar.*—Dr. B. F. Davenport wishes to call attention to his article on this subject printed in the *Journal of Analytical Chemistry*, 1, 4, in view of the fact that Prof. Leeds' attention had apparently not been called to it before writing the article printed in the September number of this journal, p. 741.



# THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

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## AN ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF WHITE LEAD.<sup>1</sup>

BY R. P. WILLIAMS.

Received September 9, 1895.

WHITE LEAD is the basis *par excellence* of white paint. For hundreds of years it has been used, mixed with linseed oil, as the main pigment where permanent, opaque, white color is desired.

Up to the present time there have been but two radically different processes of manufacture that have proved in any degree successful. These are known as the Dutch and the French processes. The English and the German are only modifications of the same principle as the others. The Dutch process is the only really successful one. I do not propose to go into the details of either of these processes, since they are well known to every chemist, but only to recall just enough of them to serve as the basis of comparison and as an introduction to the one I am to describe. Both the French and the Dutch, as well as the many modifications of them, depend upon one compound; *viz.*, lead acetate (or better, sub-acetate). This is the compound which has always been regarded as the essential first step in white lead manufacture. The fact is interesting, since white lead as a pigment has been known for more than 2,000 years, and from the earliest times it has been made by the action of acetic acid on lead. The name, Dutch process, is a

<sup>1</sup> Read at the Springfield meeting.

misnomer, as the process was introduced by the Dutch or Flemish people over 300 years ago from Italy, where it had been employed for hundreds of years previously. In fact, Pliny in the first century describes the essentials of the process, and it is said to have been employed in his country ever since his time, though, of course, on an extremely limited scale at first. Indeed Theophrastus, about 300 B. C., describes the preparation of a white pigment from lead and vinegar. This may have been the acetate, or it may have been the carbonate. The new process is a radical departure from all the old ones in not employing acetic acid at all, but in acting upon lead with nitric acid, which is generated by electricity.

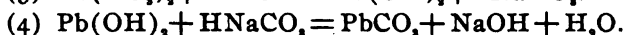
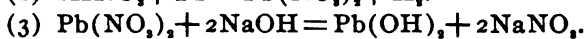
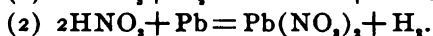
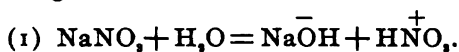
The process consists of four reactions, as given below. First, the electrical preparation of nitric acid and sodium hydroxide. Second, the action of the nitric acid on lead, forming lead nitrate. Third, the reaction of lead nitrate and sodium hydroxide to form lead hydroxide. Fourth, the combination of lead hydroxide and sodium bicarbonate to form lead carbonate.

In the first step of the process, a solution of sodium nitrate is decomposed by an electric current from a dynamo. The strength of solution required is not important, 10° Baumé, or say one pound to the gallon, being sufficient. This solution is put into a series of cells, constructed of wood, and divided into two compartments by a porous partition. At the plus electrode is fastened a pig of lead, and at the minus a sheet of copper. The solution being run in from an overhead reservoir, and the current turned on, the nitrate is decomposed according to equation (1), nitric acid collecting at the plus electrode and sodium hydroxide at the minus. The nitric acid at once attacks the lead and forms lead nitrate, which dissolves, equation (2), whereas the sodium hydroxide produces no effect on the copper at the negative pole. Finally the lead nitrate solution and the sodium hydroxide solution are drawn off separately, and mixed as desired, in quantitative proportions, in a receptacle. The result as shown in equation (3), gives lead hydroxide as a white, amorphous precipitate, and leaves sodium nitrate in solution. This is practically the original nitrate, and its regeneration shows one of the economic excellencies of the

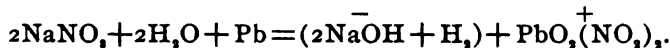
process, for the nitrate can be used over and over again, as the source of more acid.

It has been found at the experiment station, that but little additional sodium nitrate is required for a repetition of the process as complete as the original. The lead hydroxide is then filtered from the sodium nitrate. This is done automatically and continuously, by a rotary filtering device, and the sodium nitrate is pumped back into the original reservoir. The fourth step is, in some respects, the most interesting of all, and consists in adding to the lead hydroxide a solution of sodium bicarbonate (or of the normal carbonate). Reaction (4) at once takes place. It will be noted that sodium hydroxide is the product in solution, and lead carbonate the precipitate. Another beauty of this process is that the sodium hydroxide removes most of the impurities, if there are any, in the lead hydroxide; for instance, it will dissolve any salts of aluminum or of zinc, and it removes organic matter.

These impurities appear in the solution, leaving the precipitate remarkably white. Once more, this by-product, sodium hydroxide, by passing carbon dioxide into it, is converted into bicarbonate and the latter can be used again. Thus the main agent in each of the two principal steps, sodium nitrate and sodium bicarbonate, is made to do duty over and over again, with but slight additions.



It is doubtful whether (1) and (2) take place as above, but probably the reaction is as follows, since hydrogen is liberated at the minus electrode :



Let us now turn from the theoretical to the practical part of the matter. The first question which naturally arises is, will this process so beautiful in theory, and as a laboratory experiment, work on a large scale and give sufficiently practical

results to compete with the other methods of manufacture, and make it a lasting contribution to inventive science?

An experimental station was for several months in operation in Cambridge, Mass., erected and run under the direction of Mr. Arthur Benjamin Brown, the inventor of the process. This was capable of turning out some 500 pounds of white lead per day. Its success was regarded as beyond question. The cost of white lead by this process is more than covered by the gain in weight, and is but a fraction of the cost by the Dutch method. The reasons are, first, in the electrolytic process pig lead is used, as it comes from the smelting furnace. In the Dutch it has to be remelted, cast into "buckles" of definite size, and, after the action of acetic acid, from one-third to one-half is left uncorroded and has to be recast.

Second, the process is almost instantaneous, as every reaction takes place rapidly, while by the other mode from two to six months is required.

Third, in materials and labor there is great saving. No free acid is used, either acetic or nitric, and the agents sodium nitrate and bicarbonate, are used repeatedly. By the old method a plant covering a large area is filled for months with fermenting tan bark or manure, acetic acid and lead, while the process is going on, and at its completion, the product is removed with much labor, and has to be thoroughly and repeatedly washed to dissolve out any lead acetate remaining. It must be ground and reground under water, and even then is not likely to be of uniform texture. It is also a poisonous and dirty process. The electric method being continuous, is complete the same day, requires but a very small force of men, as almost all the operations are automatic, and is a clean and non-poisonous process.

The texture of the product is almost molecular in fineness, as might be expected from its being produced by replacement in the hydroxide. Hence it needs no grinding. It is so fine as to remain suspended in water for a long time, and in order to filter it a special brand of cloth had to be made, as even filter-paper would scarcely retain it.

One of the most important practical questions is: How does

paint made from electrolytic white lead compare with that made from Dutch lead in durability, opacity, and covering power? Specimens have been submitted to some of the largest dealers and painters in New England and elsewhere, and Mr. Brown, the inventor, has spent the last two years, aided by a competent corps of assistants, not only in the development of his new process, but in making thorough and systematic tests of the product. Inside and outside surfaces have been exposed to the severest extremes of weather, to the varied fumes of the laboratory, and to other crucial tests. Dutch paint and electrolytic paint have been exposed side by side for two years, and no difference can be detected in durability or opacity. The covering power of the new paint is considerably greater than that of the Dutch. Experiments vary as to the increased percentage from twelve to twenty, or even higher, but in no case was there found to be a smaller percentage.

What is the cause of such an increase? This leads us to discuss somewhat more fully the nature and composition of white lead made by the various processes. Dutch white lead consists approximately of two molecules of the carbonate to one of the hydroxide,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . This, however, appears not to be constant, as might be inferred from its mode of manufacture. Lead hydroxide is a white, amorphous substance. Lead carbonate is either a spongy transparent, globular powder, or is crystalline. Whether globular or crystalline depends upon its mode of preparation. Now certain properties of these two forms are quite different, and this difference explains the use of one and the disuse of the other form as a pigment. The globules of the one form are said to be from 0.00001 to 0.00004 of an inch in diameter. These, in the grinding of lead with linseed oil, are supposed to take up the oil, somewhat as a sponge absorbs water. The Dutch process lead is the globular variety, and to this fact has been attributed the greater body and permanence of the paint made from it than that made by most other processes. The crystalline variety of the carbonate is found not to absorb oil to anything like the same extent as the globular, no matter to what degree of fineness it is ground, the surface of the minute crystals being impervious. Half a century ago Thenard

invented the "quick process lead," or "French process." This is now carried on in Clichy, France, and some other places, and sold as "Clichy White." It is made by dissolving litharge in acetic acid and then passing into the sub-acetate of lead solution formed, carbonic acid gas. Thus is formed neutral lead carbonate. It was at first thought to be a revolutionary process, but it soon became apparent that the product did not give the capacity or body, which Dutch lead gave, and of course it lacked permanence. Made in this way the carbonate is crystalline. Under the brush it is found not to cover as much surface and not to spread as well, or it is said to lack "body," although of the same composition as the other. Other rapid processes—and there have been hosts of them—have invariably met with no better success, for the reason that the carbonate formed is the crystalline instead of the globular variety. To this fact we may mainly attribute the long continued use of Dutch process lead. The committee of experts appointed by the British Home Secretary, visited forty-six works, and found only one using the precipitation process, and three the chamber process. They say: "While some of the substitutes are cheaper to make, and far less poisonous, yet they are far from equalling the Dutch lead as a pigment. Neither can they recommend other process than the old Dutch process, for manufacturing the product."

Thus we see that until now, no cheaper method has been found for producing the globular variety. The electrolytic process *does* produce the globular kind, and a finer variety even than the Dutch, so fine in fact, that it was almost impossible to find a filter that would retain it. This probably accounts for the superiority of the electrolytic brand, as regards body and covering power over any other kind produced. Experiment shows that the pure carbonate will do as well as a mixture of carbonate and hydroxide. By the new process it is easy to make either the pure carbonate, or a mixture in any proportion, of carbonate and hydroxide. The practicability and cheapness of the electrolytic process, and the efficiency of the product being conceded, we may inquire lastly: What are the probabilities of this method being superseded by others in the future?

No other white pigment has yet been formed, or seems likely to be found, which will take the place of white lead. The two main substitutes are zinc white,  $\text{ZnO}$ , and permanent white,  $\text{BaSO}_4$ . But these do not stand the test with lead white, having far less capacity, and less covering power. Especially will they not compete with the cheapening of the latter by the new process. Hence, we must look to lead to give us the white pigment of the future.

Now what are the possible ways of making lead carbonate? There are but three common solvents of the metal; chlorine, acetic acid, nitric acid. Chlorine is at once ruled out for all practical purposes, for reasons that need not be mentioned here. Acetic acid seems to have been the substance universally employed to the present time, for getting the metals into a preliminary state for making the carbonate. As before noted, from the time of Theophrastus to the present day a host of persons in every age and many countries, have experimented and written upon the subject, all using the same method so far as concerns making lead acetate.

The inventor of the present process, worked a long time upon the acetate, but as acetic acid is an organic substance of quite complex structure, it broke up very readily under influence of an electric current, giving rise to unendurable fumes, and its use had to be abandoned. For these reasons it is safe to say that no electrolytic process is likely to employ the lead acetates. The only solvent left is therefore nitric acid. Free nitric is not likely to be used for three reasons: First, it could hardly be employed in electrolysis; Second, it would be more expensive than Chile saltpeter; Third, its reaction with lead would give rise to noxious nitric oxide fumes, and its by-product would not be re-usable. It should be said that no gases except hydrogen arise in the electrolytic process, in which the acid, as fast as liberated, combines with the lead, as may be seen from equation (2).

Now the only feasible source of nitric acid yet found, is either sodium or potassium nitrate. The former being far the more abundant and cheaper, is here as elsewhere employed, as a source of the acid, and no other nitrates are found to any extent in nature.

It would seem from what has been set forth, that not only is the process above described the most valuable and revolutionary ever invented for the manufacture of white lead, but that there is not a probability of any other process taking its place, in the near future.

This new process was invented in 1892, by Arthur Benjamin Brown, a chemist and mining engineer of Boston. It is to-day for the first time made public. The reason this has not before been done is because time was necessary to complete many details for production on a large scale, and to secure requisite patents. These are now completed, and a large company is organized to put the process into practical operation. I propose for this invention the name—The Brown Electrolytic Process.

### THE CHLORIDES OF ZIRCONIUM.<sup>1</sup>

By F. P. VENABLE.

Received September 9, 1895.

**I**N a report upon the examination of the chlorides of zirconium<sup>2</sup> it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann<sup>3</sup> the result of which made him call the substance the tetrachloride; and on repeated partial analyses of my own in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey) 39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *J. Am. Chem. Soc.*, 1894, 16, 460-475.

<sup>3</sup> *Lond. Chem. News*, 52, 233-240.



unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition along with its stability would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is  $\text{Zr}_2(\text{OH})_2\text{Cl}_7 \cdot 5\text{H}_2\text{O}$ .

UNIVERSITY OF NORTH CAROLINA,  
August, 1895.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. NO. 7.]

## THE DETERMINATION OF THE HEATING EFFECTS OF COALS.<sup>1</sup>

BY W. A. NOYES, J. R. McTAGGART, and H. W. CRAVER.<sup>2</sup>

Received September 9, 1895.

MANY determinations have been made for the purpose of comparing the heating effect of coals as determined by the calorimeter with that calculated from analyses. Scheurer-Kestner, who seems to have been the first to show that the results obtained in the two ways do not agree, publishes results obtained with the calorimeter of Favre and Silbermann, which differ, in some cases, by ten per cent. from those calculated by Dulong's formula and are uniformly higher.<sup>3</sup> In a later paper<sup>4</sup> he states that he finds lower results with Bertholet's bomb but still results that differ from those calculated.

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> The work of which this paper gives an account formed the basis of theses presented to the faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science.

<sup>3</sup> *Compt. rend.*, 106, 1092, 1160, 1230.

<sup>4</sup> *Ibid.*, 112, 233.

Ferd. Fischer claims repeatedly in the *Zeitschrift für angewandte Chemie* and elsewhere that the calorimeter results differ from the calculated heating effect, but admits that the latter may answer for most technical purposes.

Hempel<sup>1</sup> states that the results calculated from careful analyses do not differ more than one or two per cent. from those of the calorimeter and considers that larger differences sometimes found have been due to careless work. He gives six cases of fair agreement, but one which shows a difference of six per cent.

Alexejew<sup>2</sup> gives one case in which the calorimeter result is three and eight-tenths per cent. higher than that calculated.

Scheurer-Kestner<sup>3</sup> has compared the results obtained with Thompson's calorimeter (burning with potassium nitrate and potassium chlorate) with those given by the calorimeter of Favre and Silbermann and finds a maximum difference of three and a half per cent. In using Thompson's method, however, he applies a constant plus correction of fifteen per cent., which F. Fischer criticises as very unreliable.

W. Thompson<sup>4</sup> describes a simple calorimeter which he has devised and gives results obtained with twelve samples of coal. In seven cases the results are lower, in two cases they are the same, and in three cases they are higher than those calculated. F. Fischer<sup>5</sup> criticises these results, saying that the coals were probably not completely burned.

Barrus has described<sup>6</sup> a calorimeter which he appears to have copied from that of W. Thompson.

C. v. John and H. B. Fuller<sup>7</sup> have made a series of comparisons of Berthier's test (reduction of litharge) with the results calculated from analyses. The latter give, in some cases, 900 calories more than the former.

So far as we are aware, no comparisons of this kind have been made with American coals. The work here described was un-

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 393.

<sup>2</sup> *Ber. d. Chem. Ges.*, 19, 1557.

<sup>3</sup> *Compt. rend.*, 106, 941.

<sup>4</sup> *J. Soc. Chem. Ind.*, 5, 581, and 8, 525.

<sup>5</sup> *Jahrb. chem. Tech.*, 1889, 9.

<sup>6</sup> *Trans. Mech. Eng.*, 14, 816.

<sup>7</sup> *Ztschr. angew. Chem.*, 1893, 285.

dertaken for the purpose of comparing the results obtained with Hempel's calorimeter with those calculated from analyses and those obtained by Berthier's test. Six specimens of representative Indiana coals were used, as follows: Brazil Block from Brazil, Lancaster Block from Clay Co., Shelburn coal from Shelburn, two samples from the mines of the New Pittsburg Coal Co. at Alum Cave, and a sample of mine screenings used in the shops of the Rose Polytechnic Institute. The first two are known locally as "block" coals and are non-coking. The others are known as bituminous and are coking coals.

#### ANALYSES.

The analyses were made as follows:

1. *Moisture*.—One gram of the coal was dried in a toluene-bath (about 105°) for one hour.

2. *Ash*.—The residue of (1) was ignited over a Bunsen burner, at first with a very low flame, till the carbon was completely burned.

3. *Fixed Carbon*.—One gram of fresh coal was placed in a covered platinum crucible and heated with the full flame of a Bunsen burner for just seven minutes. The residue less the ash is the "fixed carbon."

4. *Volatile Combustible Matter*.—The loss of weight in (3) less the moisture is volatile combustible matter.

The above determinations are, of course, of no value for the calculation of the heating effect but give some indication of the character of the coal.

5. *Carbon and Hydrogen*.—About two-tenths gram of the coal was burned in a current of oxygen in a hard glass tube containing copper oxide and lead chromate.

6. *Nitrogen*.—This was determined with soda-lime.

7. *Sulphur*.—Determinations were made by Eschka's method, using potassium carbonate and magnesium oxide, by the method of Carius and by the use of sodium peroxide, as follows: one-half gram of the coal was weighed out in a platinum dish holding about fifty cc. and three grams of sodium peroxide and a little water were added. The whole was evaporated to dryness and ignited. After adding two grams of sodium peroxide and more water the evaporation and ignition were repeated. The mass was then

boiled with water, the solution filtered, acidified, and precipitated as usual. The barium sulphate was purified by fusion with sodium carbonate. The results obtained by this method agreed fairly well with those obtained by Eschka's method, but the results of Carius' method were mostly higher. As a comparison of methods was not part of our plan, the average of the results obtained by Eschka's method are given in the table.

8. *Oxygen*.—In most coal analyses the oxygen has been calculated by subtracting the other constituents, including the ash, from 100. Where the sulphur is low this introduces but a slight error. But with sulphur so high as in some of these coals the error is quite appreciable. The sulphur is mostly present in the form of pyrites and it has been assumed that this is burned to sulphur dioxide and ferric oxide. Accordingly, for the calculation of the oxygen, a correction has been applied to the ash by adding to it five-eighths of the weight of the sulphur present.

The quantities given in the following table are in every case, the average of at least two results obtained by different persons. Where the agreement was not fairly close, a larger number of determinations has been made, and results differing too far from the mean have been rejected. For the results finally used, the average variation from the mean is 0.08 per cent. for carbon, and 0.18 per cent. for hydrogen. These differences correspond to a difference of fifty-seven calories, or about nine-tenths per cent. of the calculated heating effect.

The heating effect is calculated for the coal burned to vapor of water by the formula  $8080C + 28800(H - \frac{1}{8}O) + 1582Fe + 2162S$ , where C, Fe, etc., are the amounts of each element present. As will be seen from the table, the heating effect of the iron and sulphur is quite important in some of these coals.

#### CALORIMETRIC DETERMINATIONS.

The calorimeter used was that described by Hempel.<sup>1</sup> The powdered coal was compressed into cylinders, through which a fine iron wire passed. This wire was weighed, and it was assumed that it gave one-fifth as much heat by its combustion, as the same weight of coal. The autoclave was filled with oxy-

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 393. See also Hempel's *Gas Analysis*, translated by L. M. Dennis.

gen, by generating the gas from a mixture of potassium chlorate and manganese dioxide. The temperatures were read by means of a telescope, the thermometer being graduated into fifths. The highest point reached by the thermometer, was used for the calculation. As the rise in temperature was only about five degrees, and the same method was used in determining the water equivalent of the calorimeter, the error due to radiation must have been small. The water used was delivered from a measuring flask, and was found by direct weight to be 997.8 grams. The water equivalent of the autoclave and calorimeter was determined by burning pure sugar charcoal as directed by Hempel. Six determinations gave an average value for the whole, including the water used of 1337.5 grams, with a probable error of five and nine-tenths grams or 0.45 per cent.

At least three determinations were made with each coal. The average difference of the values obtained from the mean for a given coal, was thirty-two calories, or one-half per cent.

The water formed by the combustion in the calorimeter condenses, of course, to liquid water, and, assuming that the average temperature of the calorimeter is  $26^{\circ}$ , a correction of 610 calories per gram of water formed must be subtracted to find the heating effect when burned to vapor of water. The results given in the table have been corrected in this manner.

#### BERTHIER'S TEST.

This was made as follows: One gram of the coal was intimately mixed with forty grams of litharge and the mixture put in a Battersea C crucible, seven and a half cm. deep, and four and a half cm. internal diameter, and covered with a layer of salt. The covered crucible was then placed in a *hot* gas furnace and heated for fifteen or twenty minutes. The crucible was then taken out, tapped to collect the lead, cooled, broken, and the lead button cleaned and weighed.

Theoretically, one gram of lead should correspond to a heating effect in the coal of 234 calories. The results calculated with this factor are, however, about twelve per cent. too low. The average of the results obtained, give an empirical factor of 268.3 calories per gram of lead. The results given in the table have been calculated with this empirical factor.

At least three fairly concordant determinations were obtained for each coal. A few results differing from this mean by more than one-half a gram of lead were rejected. The average difference of the results from the mean for a given coal, was 0.11 gram, which corresponds to twenty-nine calories or about 0.45 per cent.

The following table gives the results of the analyses and other determinations. The differences between the other determinations and those made with the calorimeter are given in per cents.

	New Pittsburgh A.	New Pittsburgh B.	Lancaster.	Brazil.	Shelburn.	Shop.
Moisture .....	6.83	5.89	12.66	8.98	8.63	2.36
Volatile combustible matter..	39.92	42.23	37.44	34.49	38.82	31.11
Fixed carbon .....	39.93	40.40	47.22	50.30	43.45	42.44
Ash .....	13.31	11.48	2.68	6.23	9.05	24.09
Carbon .....	62.88	65.26	71.41	70.50	66.86	57.32
Hydrogen .....	5.07	5.17	5.56	4.76	5.30	4.56
Nitrogen .....	1.01	1.17	1.54	1.36	1.50	1.44
Oxygen .....	13.06	13.25	18.42	16.29	15.69	9.93
Ash (corrected).....	17.98	15.15	3.07	7.09	10.65	26.75
Sulphur .....	7.46	5.88	0.62	1.39	2.57	4.25
Iron, calculated .....	6.53	5.14	0.54	1.22	2.25	3.72
Calories per gram, calc'ted C	5081.	5272.	5770.	5696.	5402.	4632.
"    "    "    "    H	991.	1011.	939.	784.	962.	956.
"    "    "    "    S	161.	127.	13.	30.	55.	92.
"    "    "    "    Fe	103.	81.	9.	19.	36.	59.
Total	6336.	6491.	6731.	6529.	6455.	5739.
Difference, per cent.....	+2.6	+1.2	+0.4	-4.6	-1.2	-1.2
Calories per gram, Berthier's						
test, factor 268.3.....	6307.	6471.	6831.	6689.	6461.	5726.
Difference, per cent.....	+2.1	+0.9	+1.9	-2.3	-1.1	-1.4
Calories per gram, calorimeter	6175.	6415.	6703.	6846.	6532.	5806.

In discussing the results, it is worth while to notice that, so far as indicated by the agreement of duplicate determinations, about the same degree of uncertainty attaches to the calorimetric determinations and to the litharge test, while the uncertainty of the analysis is about twice as great. It is noticeable that the results calculated from the analyses, and those given by

Berthier's test, agree better with each other than either agree with the calorimeter results.

On the average Berthier's test, when the empirical factor is used, appears to be more reliable than the results calculated from the analyses.

While the differences between the results obtained by different methods are not very great, they are certainly greater than can be accounted for by the errors of the work. In the case of two of the most important coals, the Lancaster and Brazil black, the relative value of the coals as given by the calorimeter, is reversed as given by the analyses and by Berthier's test. There can be little doubt that the calorimeter gives most accurately the relative heating value of these coals.

Attempts to make determinations with anthracite coals were unsuccessful, because it was found impossible to compress it into cylinders, and we have not yet been able to burn it in the form of a powder.

Some attempts have also been made to use the calorimeter of Barrus,<sup>1</sup> but a deposit of carbon was always formed, and the results appeared to be entirely unreliable. It is probable that the results would be more satisfactory with anthracite coals.

TERRE HAUTE,  
INDIANA.

## TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES WITH NOTES ON SOME NEW REACTIONS.\*

BY CABELL WHITEHEAD.

Received Sept. 9, 1895.

**T**ELLURIUM which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent, that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade

<sup>1</sup> Trans. Mech. Eng., 14, 816. See als W. Thompson, *loc. cit.*

\*Read at the Springfield meeting

telluride ores, is a problem which, up to the present time, has baffled the skill of the metallurgists of the world. A few of the difficulties may be mentioned as follows: Tellurides do not give up their gold to mercury, cyanide or chlorine, they concentrate badly, a large percentage of the value being lost as slimes. They are difficult to roast, on account of their low melting-point and the loss of gold, during the removal of the tellurium. The usual course is to smelt this class of ore either with lead or copper ores. It is to the latter method I will call especial attention in this paper.

In order to work the copper ores of the west economically, they are smelted with gold and silver-bearing ores which act as flux, and also enrich the matte produced to a point where the cost of refining the copper is more than covered by the value of the precious metals contained. In this way large amounts of tellurium enter the matte. These mattes are Bessemerized in the west, and copper brought east to be refined by electrolysis. It contains from 98.5 to 99.5 per cent. copper, about 100 ounces of silver, and three-tenths ounce of gold per ton. The impurities are arsenic, antimony, lead, bismuth, tellurium and selenium. The average amount of tellurium is not far from 0.04 per cent. or 0.8 of a pound per ton. With the possible exception of the native copper of Lake Superior, it is doubtful if any copper produced is free from tellurium; this is certainly true of that from sulphide ores. I have already described a method for estimating the tellurium under these circumstances.<sup>1</sup>

The electric refining of such copper is carried on at Anaconda and at the Boston and Montana Copper Co. works at Great Falls, Montana; the Baltimore Electric Refining Co., Baltimore, Maryland; the Bridgeport Copper Co., Bridgeport, Conn., and the Ansonia Refining Co., Ansonia, Connecticut; the Central Falls Electric Refining Co., Central Falls, Rhode Island; the Washburn and Moen Co., Worcester, Mass. and perhaps others.

In the Hayden process a bath of dilute copper sulphate, acidified with sulphuric acid is employed, in which is inserted an anode of rolled black copper and a cathode from a strip of pure copper, each being connected with the electric generator, while

<sup>1</sup>*J. Am. Chem. Soc.*, 17, 280, 1895.



disconnected plates of black copper are suspended in the bath between the two electrodes. When the current is on, solution takes place, not only at the anode but on all the disconnected plates interposed between the electrodes, and what is more interesting, this solution takes place on those surfaces of these plates which face the negative electrode, while the deposition of the pure copper takes place on the surface of the adjacent plate which faces the positive electrode. When the copper goes into the solution in its bath small amounts of some of the impurities in the copper enter into solution with it, but the greater portion remains either in the metallic state or are converted into oxides or basic salts which fall to the bottom of the bath where they form a black slimy residue.

The commercial refining of these residues is carried out as follows:

After screening out the coarser copper, the slimes are boiled with a twenty per cent. solution of sulphuric acid in a lead-lined tank by live steam, air being drawn in with the steam by means of a peculiar injector. During this boiling, practically all of the antimony, arsenic and bismuth salts, together with copper in the oxidized condition and that small portion of metallic copper which has been oxidized by the injected air go into solution.

After about one hour's boiling, a solution of silver sulphate is run in and steam applied for some minutes whereby according to the reaction  $\text{Cu} + \text{Ag}_2\text{SO}_4 = \text{CuSO}_4 + \text{Ag}_2$ , the metallic copper still remaining is rapidly and completely converted into copper sulphate. Any excess of silver sulphate is removed by the addition of a fresh portion of slimes, when the solution is drawn off and the residue washed until free from copper salts. This residue, which has now lost the slimy, adhesive properties which characterized it and which consists of gold, silver, tellurium, and lead sulphate is pressed on a filter press. The pressed cakes are dried in an oven and then melted in a furnace, having a bed made of Portland cement, which is so arranged that a blast may be turned on. This quickly removes all but a trace of the lead present, together with portions of the tellurium and selenium.

The resulting bullion is poured into shoe-bars, weighing about 300 ounces each, it is about 950 fine, in silver and ten parts of

gold. When cool these bars are dissolved in hot sulphuric acid, in a cast iron kettle, and when solution is complete the liquid is allowed to cool and settle for several hours, during which the gold falls to the bottom and the tellurium crystallizes out in white lustrous crystals of tellurous oxide. The first portion of the clear liquid is drawn off and precipitated by metallic copper, and the silver melted into bars 990 fine. The remainder is used in treating a fresh portion of the slimes.

The gold and the tellurous oxide are allowed to accumulate in the kettle until several hundred ounces are at hand, when they are removed and washed with dilute sulphuric acid and water, to remove silver, copper sulphate and tellurous oxide, and afterwards boiled in a small kettle with concentrated sulphuric acid to remove the remaining portion of silver and tellurium. When cool, and the gold has settled, the acid is again drawn off and the residue washed until free from tellurium and silver sulphates. The gold is now melted with borax and niter, by which any remaining traces of lead and tellurium are oxidized and slagged off, leaving fine gold, over 990 fine, the impurity being silver.

The washings from the gold residue contain the tellurium as tellurous oxide or tellurous sulphate. The tellurium may be obtained from these in two ways, after the removal of the silver as chloride. First, by precipitation with copper; second, by passing sulphur dioxide through the solution. It is better to use the first method, as large quantities of sulphur dioxide are very disagreeable to handle, and as the tellurium thus precipitated in the presence of copper is not pure and requires a further treatment. The metal used in this work was produced by inserting bars of copper into the solution and boiling with steam, a precipitate of cuprous telluride being obtained as a black powder. This was dried and then boiled with a five per cent. solution of sulphuric acid to remove the copper which had been oxidized during the drying process. After filtering, the mass is again moistened with five per cent. sulphuric acid and subjected to atmospheric oxidation with frequent stirring, then boiled again with more sulphuric acid and washed, this process is repeated until the copper is eventually very completely removed. Any copper left will combine with tellurium when fused and

cause loss. The residue is now dried, mixed with three times its weight of sodium carbonate, and one-fourth its weight of charcoal, melted in a French clay crucible to quiet fusion, brought almost to a white heat, and the melt poured into a suitable mold. The cooled mass is crushed to a powder and the sodium telluride formed, dissolved out with boiled water; a great amount of heat is developed during the solution. The solution thus produced, which possesses a rich port wine color, is filtered off, and the tellurium precipitated in the metallic state, by the passage of a current of air, as a fine gray powder, looking not unlike finely powdered galena. The tellurium is filtered and boiled with dilute hydrochloric acid, to remove traces of iron, alumina, etc., washed and boiled for several hours, with a concentrated solution of potassium cyanide which removes selenium and most of the gold present. After drying, the tellurium is melted, without flux, in a French clay pot, the fine particles are made to run together by stirring, only a low temperature is necessary and the loss by volatilization is small. The metal still contains traces of impurities, the chief of which is gold. This would indicate that sodium telluride is a solvent of metallic gold, but this has not yet been proven. The tellurium is further purified by distillation in hydrogen gas.

#### NEW REACTIONS OF THE SALTS OF TELLURIUM.

If to a solution of the sodium or potassium tellurite is added a solution of an ammonium salt, such as the chloride or nitrate, a white precipitate is thrown down, which on boiling becomes granular.



A small amount of tellurium dioxide or a metal which can be precipitated by sulphur dioxide remains in solution. It is the intention of the writer as soon as possible to examine and compare the properties of the metal from this fractional precipitation. While it is probable that tellurium oxide is slightly soluble in the alkali salts formed, which would explain incomplete precipitation, in view of the growing belief in the compound nature of tellurium, this reaction is deemed worthy of further investigation.

In an effort to purify tellurium, based upon the well-known property of hydrogen telluride of precipitating many of the

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metals from solution, the following reaction was observed, in addition to the one expected:  $\text{TeCl}_4 + 2\text{H}_2\text{Te} = 3\text{Te} + 4\text{HCl}$ . By passing this gas for some time into a solution of tellurium chloride, made slightly acid with hydrochloric acid, there was obtained a precipitate of tellurium and tellurides and a solution, from which sulphur dioxide threw down a precipitate of tellurium. After distillation in hydrogen I propose to determine the atomic weight of this purified metal.

When potassium ferrocyanide is added to tellurium chloride no change is observed at first but after a few hours Prussian blue is formed in large quantities.

### ALUMINUM TELLURIDE.

Tellurium when heated with aluminum combines with explosive violence, forming a chocolate colored, difficultly fusible compound having the following composition by analysis.

	Per cent.
Aluminum .....	12.78
Tellurium .....	87.22
	<hr/>
	100.00

This corresponds closely to the formula  $\text{Al}_2\text{Te}_3$ , which requires

	Per cent.
Aluminum .....	12.58
Tellurium .....	87.42
	<hr/>
	100.00

The violent chemical action attending its formation, joined with the fact that its composition remains constant, even in the presence of a large excess of aluminum, would indicate a true chemical combination and not an alloy, in the accepted sense. It is hard and brittle, can be easily ground to powder. When exposed to moist air it is slowly decomposed with the liberation of hydrogen telluride. When thrown into water hydrogen telluride is rapidly given off according to the following reaction:  $\text{Al}_2\text{Te}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{Te}$  which corresponds to the well known sulphur reaction  $\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{S}$ . While comparing these two reactions it may be noted that hydrogen telluride is much more easily decomposed by oxygen than hydrogen sulphide. For example in treating aluminum telluride with

water which has not been boiled fully one-half of the tellurium remains as metal:  $\text{H}_2\text{Te} + \text{O} = \text{H}_2\text{O} + \text{Te}$ . When treated with ninety-five per cent. alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts as it does not decompose in the air so quickly as the alkali tellurides.

#### SEPARATION FROM COPPER BY THE ELECTRIC CURRENT.

Tellurium is easily deposited by the current, either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about three grams of potassium cyanide for each gram of copper present. With this solution, a current such as is used for depositing copper, will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours, the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough, none of it will adhere to the cathode.

COLUMBIAN UNIVERSITY, WASHINGTON, D. C.

### THE ELECTROLYTIC REDUCTION OF PARANITRO COMPOUNDS IN SULPHURIC ACID SOLUTION.<sup>1</sup>

BY ARTHUR A. NOYES AND JOHN T. DORRANCE.

Received September 9, 1895.

#### INTRODUCTION.

It was shown some time ago by Noyes and Clement<sup>2</sup> that nitrobenzene in sulphuric acid solution is transformed by electrolytic hydrogen into paraamidophenolsulphonic acid. It has since been proved by the extended investigations of Gattermann and his students<sup>3</sup> that this behavior is characteristic of aromatic nitro compounds in general, one of the oxygen atoms

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *Ber. d. chem. Ges.*, 26, 990.

<sup>3</sup> *Ibid.*, 26, 1844, 2810; 27, 1927.

of the nitro group always migrating during the reduction to the para position with the production of a hydroxyl group. It is evident, however, that this cannot take place when the position para to the nitro group<sup>1</sup> is occupied by another element or group than hydrogen. The purpose of our investigation was to determine the nature of the reduction-products of a number of such compounds with the view of ascertaining any general principle that may exist. Only three such para compounds have been previously studied, namely, paranitrotoluene and paranitroorthotoluidine by Gattermann<sup>1</sup> and paranitrobenzoic acid by Noyes and Clement.<sup>2</sup> We have now investigated three additional ones, paranitraniline, paranitrophenol, and parachlornitrobenzene.

#### THE METHOD OF REDUCTION.

The method of carrying out the reduction was essentially the same in all cases. The apparatus consisted of a small beaker, to the sides of which a large platinum electrode was closely fitted, and in which was placed a cylindrical porous cup containing a small platinum electrode. Concentrated sulphuric acid was placed within the cup at the start, and small quantities of diluted acid were occasionally added during the electrolysis to prevent the acid from becoming fuming. The solution to be electrolyzed was placed outside; it was prepared by dissolving twenty or thirty grams of the substance in two and a half to three times its weight of strong sulphuric acid. A current of one or two amperes was passed through for forty or fifty hours.

The reduction-product precipitated either during the electrolysis or after cooling. It was filtered out upon a hardened filter with the aid of suction and dried by spreading on porous plates. The filtrate was diluted with an equal bulk of water, and any further precipitate added to the original one. The subsequent purification varied in the different cases, and will be described under the separate substances.

#### REDUCTION OF PARANITRANILINE.

The paranitraniline used was in part a Kahlbaum preparation and was in part prepared by ourselves by the method given by

<sup>1</sup> *Ibid.* 26, 1850, 1852.

<sup>2</sup> *Am. Chem. J.*, 16, 511.

Nölting and Collin.<sup>1</sup> It gave the correct melting-point of 146°.

The reduction-product was isolated by extracting the precipitate dried on the porous plates with boiling water, boiling the solution with animal charcoal, filtering, and causing to crystallize by cooling.

It was found to consist of paradiamidobenzene sulphate. It was very difficultly soluble in cold water.<sup>2</sup> Its solution was colored purple by ferric chloride, and it gave the following results on analysis:

0.2193, 0.2847, and 0.3581 gram substance gave respectively 0.0985, 0.1262, and 0.1638 gram water and 0.2822, 0.3672, and 0.4605 gram carbon dioxide.

0.3147, 0.2077, 0.3938, and 0.4525 gram substance gave respectively 0.3481, 0.2340, 0.4363, and 0.5066 gram barium sulphate.

	I.	Found.		IV.	Calculated for $C_6H_{10}N_2SO_4$ .
Carbon.....	35.10	35.18	35.08	....	34.94
Hydrogen.....	4.99	4.92	5.08	....	4.85
Sulphur trioxide	38.32	38.68	38.04	38.44	38.84

#### REDUCTION OF PARANITROPHENOL.

A sample of the substance from Kahlbaum having the correct melting-point (113°) was employed.

The reduction-product was practically insoluble even in boiling water, but dissolved readily in sodium hydroxide or carbonate. It was purified by dissolving in the latter, filtering, and precipitating immediately with hydrochloric acid. The precipitate was washed successively with water, alcohol, and ether, and dried at 125°. Twelve grams were obtained from thirty grams of nitrophenol.

The physical and chemical properties and the analysis of the body established its identity as paraamidophenolsulphonic acid, It reduced silver nitrate solution in the cold with the production of a purple color, and turned brown rapidly in alkaline solution owing to oxidation. It was decomposed by heating with strong

<sup>1</sup> *Ber. d. chem. Ges.*, 17, 262.

<sup>2</sup> Contradictory statements exist in the literature as to the solubility of this salt. Nietski, in *Ber. d. chem. Ges.*, 11, 1098, states that it is readily soluble. Vignon, in *Bull. Soc. Chim.*, 50, 153, that it requires 714 parts of water at 15°. The latter statement is, according to our experience, the correct one.

hydrochloric acid in a closed tube to  $180^{\circ}$ ; the hydrochlorate of the base crystallized out upon cooling, and from this, by the addition of potash, the base itself was set free. Like paraamidophenol, it melted at  $183^{\circ}$ , undergoing decomposition. It also showed the characteristic color reactions of that substance with chloride of lime and ferric chloride.

The analysis of the sulphonic acid gave the following results:

0.2361 gram substance gave 0.0879 gram water and 0.3295 gram carbon dioxide.

	Found.	Calculated for $C_6H_5.NH_2.OH.SO_3H$ .
Carbon .....	38.06	38.08
Hydrogen .....	4.13	3.70

#### REDUCTION OF PARACHLORNITROBENZENE.

A Kahlbaum preparation (melting-point  $83^{\circ}$ ) was employed in this case also. The reduction-product proved to be a sulphonic acid, and was purified exactly as that obtained from the reduction of nitrophenol. It was first tested qualitatively for chlorine and found to contain none. It exhibited in fact all the characteristic properties of paraamidophenolsulphonic acid, being almost insoluble in hot water, oxidizing very rapidly in alkaline solution, and readily reducing silver nitrate solution. It was subjected to just the same treatment as the reduction-product of the nitrophenol with identical results. In addition to the confirmatory tests described under that substance, the diacetyl derivative of the base was prepared by boiling with acetic anhydride, and this was found to melt at  $149^{\circ}$ . Diacetyl-paraamidophenol melts according to Ladenburg at  $150^{\circ}$ – $151^{\circ}$  C.

The sulphonic acid gave the following results on analysis:

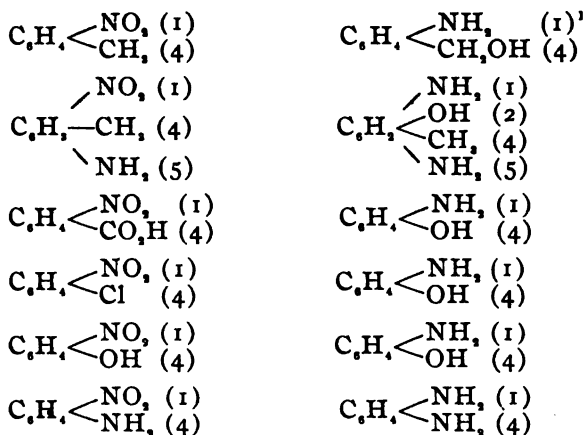
0.2912 gram substance gave 0.1002 gram water and 0.4059 gram carbon dioxide.

	Found.	Calculated for $C_6H_5.NH_2.OH.SO_3H$ .
Carbon .....	38.02	38.09
Hydrogen .....	3.90	3.70

#### SUMMARY OF THE RESULTS.

The paranitro compounds, which up to the present time have been submitted to electrolytic reduction are tabulated below together with their reduction-products:





The most striking of the results are those obtained with the paranitrobenzoic acid and with the parachloronitrobenzene, the group para to the nitro group being driven out in each case. It seems not improbable that this behavior is a general characteristic of nitro compounds with negative para groups, but an investigation of others would be needed in order to establish it as a fact.

It is also worthy of note that, contrary to what might be expected, in only one of the six cases, that of the nitrotoluidine, does the oxygen atom display any tendency to migrate to any other than the para position.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.

## PERIODIDES OF PYRIDINE.<sup>2</sup>

BY A. B. PRESCOTT AND P. F. TROWBRIDGE.

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### PYRIDINE ALKYL PERIODIDES.

1. *Pyridine Methyl Pentiodide*.—This was obtained in the manner given in detail below, very satisfactorily in preparation I, and with slight impurity in two other preparations, II and III, by different ways, through separation from other periodides.

<sup>1</sup> The substance isolated was a condensation-product of this with a second molecule of nitrotoluene; but this is undoubtedly the primary reduction-product.

<sup>2</sup> Read at the Springfield meeting of the American Association for the Advancement of Science, September 2, 1895.

Preparation I is in greenish-black long needles of very dark green luster, some of the crystals being nearly two inches in length. The melting-point is  $47.5^{\circ}\text{C}$ .<sup>1</sup>

Preparation II is of small quantity, in greenish-black crystals, very hard and compact, melting at  $47^{\circ}\text{C}$ .

Preparation III is in crystals exactly like I, melting at  $47^{\circ}\text{C}$ ., by recrystallization in alcohol from a greenish-black crystalline powder, the latter being stable and melting at  $43^{\circ}\text{C}$ . The analysis of III was obtained only from this powder, before the final crystallization. These three preparations are, alike, so far stable that after keeping eight months in glass-stoppered bottles, most of the time in the dark, the glass is but just perceptibly stained with iodine liberated from decomposition.

The analyses of the methyl pentiodide, by methods detailed further on, gave results as follows:

	Calculated for $\text{C}_5\text{H}_5\text{N} \cdot \text{CH}_3\text{I}_5$	I.	Found. II.	III.
Iodine total .....	87.06	86.74	....	86.69
Iodine by titration ....	69.65	68.87	69.83	69.55

2. *Pyridine Methyl Diiodide*.—Obtained through different ways, as stated later, in two preparations. I is in reddish-brown crystals, thick plates, compact in clusters. Some crystals are an inch long and a fourth of an inch wide. Melting-point,  $91.5^{\circ}\text{C}$ . The crystals are very stable. On eight months' standing there are no perceptible results of decomposition. II is in red interlaced fine needles of good length, the last previous crystallization having been in dark-red sheaf-form clusters of great beauty. Melting-point,  $91.0^{\circ}\text{C}$ . In stability II is equal to I.

The analyses, with duplicates as specified later, gave the following:

	Calculated for $\text{C}_5\text{H}_5\text{N} \cdot \text{CH}_2\text{I}_2$	I.	Found. II.
Iodine total .....	72.91	72.88	72.33
Iodine by titration .....	36.55	36.97	36.40

3. *Pyridine Methyl Triiodide*.—Obtained in three preparations, each from a separate recrystallization out of a common mother-

<sup>1</sup> Measurements of the crystals, and various optical determinations, as well as work by other physical methods, especially such as bear upon molecular weight and constitution, are reserved together for a continued investigation of these bodies.

liquor, that of II of the methyl diiodide. Again it is obtained in the first crystallization by another method, that for IV. I is in dark-red fine needles, quite perfect in outline and partly clustered in certain sheaves characteristic of the earlier crystallizations of this triiodide. Melting-point,  $50^{\circ}$  C. Perfectly stable.

II shows dark-red needles, the previous crystallization having been merely a loose crystalline mass. Obtained perfectly stable, with melting-point of  $50^{\circ}$  C.

III is dark-red needle clusters of a certain exact sheaf-form appearing illusively in several earlier crystallizations. But a small quantity was obtained, with a melting-point of  $49^{\circ}$ – $50^{\circ}$  C.

IV, perhaps the most perfect, is in very dark red or reddish-black plates with needles, perfectly stable, and melting at  $48^{\circ}$  C.

The results in analysis have been these :

	Calculated for $C_5H_5N.CH_2I.I_2$ .	I.	Found. II.	III.	IV.
Iodine total.....	80.14	79.32	79.22	....	78.70
Iodine by titration.....	53.43	53.08	51.52	52.75	53.15

4. A product was obtained of seeming distinct character, in composition and melting-point nearly approaching the pentaiodide, but with the elemental figures of a tetrapentaiodide, that is, dipyridinedimethylenneaiodide. It is reserved for further work. It is in greenish-black, lustrous, long needles, well defined, of a melting-point of  $44^{\circ}$  C. The total iodine in three successive determinations was found to be, respectively, 85.83, 85.88, and 85.83 per cent.; calculation for  $(C_5H_5N.CH_2I)_2I_4$ , giving 85.68 per cent., and for  $C_5H_5N.CH_2I.I_2$ , 87.06 per cent. The iodine by titration was found to be 67.52, 67.08, 67.02, and 66.69; calculation giving for these formulas, respectively, 66.45 and 69.65 per cent.

5. *Pyridine Methyl Octaiodide*.—This product is named provisionally, one fairly satisfactory preparation of it being obtained, a second preparation having the requisite composition but (possibly from its more compact crystallization) having a higher melting-point, and a third preparation, while agreeing in melting-point with the first, falling too low in percentages of iodine. The preparation, detailed below, was instituted in the hope of obtaining the enneaiodide. I, by recrystallization from alcohol below

$0^{\circ}$  C., is greenish-black, in both plates and needles, melts at about  $26^{\circ}$  C., and is fairly stable when kept at about  $15^{\circ}$  C. or below. II is in crystals of the same color as those of I, but more slowly formed and more compact, consisting of flat needles, some of them an inch long, with melting-point of about  $41^{\circ}$  C.. III was imperfectly crystallized, rather solidified in a crystalline mass, of the color of I, and melting at  $25^{\circ}$  C. We do not include III among the determinate preparations. It gave of total iodine, 90.36 per cent., and of iodine by titration 78.41 per cent., both figures being low for the octaiodide and much too high for the heptaiodide.

	Calculated for $C_6H_5N.CH_2I.I_7$ .	I.	Found. II.
Total iodine.....	91.51	90.79	90.99
Iodine by titration .....	80.07	79.82	80.13

6. *Pyridine Ethyl Triiodide*.—Obtained, as specified under the account of preparations, from liquid secondary products corresponding to those which gave the three samples of the pyridine methyl triiodide, in lustrous greenish-black needles, well defined, stable through exposure to the air, and melting at  $49^{\circ}$  C. In the analysis, two determinations by silver iodide gave for iodine 78.389 and 78.388. Three titrations with the thiosulphate gave for iodine 52.784, 52.612 and 52.616. Inasmuch as the mother liquids have been found to contain higher periodides, it is evident that these crystals are not wholly freed from mother liquid.

	Calculated for $C_6H_5N.C_2H_5I.I_3$ .	Found.
Iodine total.....	77.85	78.39
Iodine by titration.....	51.90	52.67

7. Higher ethyl periodides of pyridine, in nearly black crystals melting below  $10^{\circ}$  C., were indicated from treatment of the primary oil-like product, though not yet obtained in purity, as stated under the preparation of the triiodide.

*Methods of Preparation*.—The methyl periodides of pyridine are best obtained, first, by adding the methyl normal iodide of pyridine to dissolved iodine. We have also obtained several pyridine methyl periodides; second, by adding pyridine to a solution of methyl iodide and iodine. We have found, however, as stated further on, that in the latter way there is formed some proportion of a pyridine periodide destitute of methyl, though

the avidity of pyridine for methyl iodide ensures a considerable proportion of methyl periodides. For pyridine ethyl periodides the second way would not promise formative results at all owing to the tardy addition of ethyl iodide to pyridine. The normal pyridine alkyl iodides used were prepared for the purpose, and had the properties specified in another paper by one of us (P), in which, also, is a statement of the constants of the pyridine used in these preparations. In adding the pyridine alkyl normal iodide to iodine, the latter was taken in the proportion to make the particular periodide desired, but other periodides would appear as subordinate products. As to just how much effect the relative quantity of iodine added exerts upon the extent of iodine combination, further investigation is now in progress.

The preparation of pyridine methyl pentiodide was done as follows: Eighteen grams of pyridine methyl iodide dissolved in a little alcohol were added to fifty grams of iodine previously dissolved in 200 cc. of alcohol, the solutions being taken at low temperature. A dark green oil-like liquid, thick and cohesive, at once separated in abundance at the bottom. The thin alcoholic liquid above was decanted off and the oil set aside at temperature several degrees below  $0^{\circ}\text{C.}$ , when it shortly solidified in crystals, not melting at  $25^{\circ}\text{C.}$  These were dissolved in warm alcohol, and the solution set aside at about  $-5^{\circ}\text{C.}$ , when crystals of preparation I appeared. They were dried over sulphuric acid to a constant weight, for analysis and determination of the melting-point. This periodide was undoubtedly obtained in its amorphous oil-like state by O. Lange in 1885<sup>1</sup> while engaged in obtaining decomposition products of pyridine methyl iodide by Ladenburg's process. He reported obtaining the heavy dark-green oil, which would not solidify on standing for a day, and which he apparently did not analyse.<sup>2</sup> III of the methyl pentiodide was obtained by treating a part of the first crystalline form of the methyl octaiodide before described, with ether, which

<sup>1</sup>On Picolines, *Ber. d. Chem. Ges.* 18, 3436.

<sup>2</sup>It was in following Lange that this preparation I of the methyl pentiodide was first undertaken, and the "oil" obtained. After fruitless attempts to crystallize it from various solvents, it was abandoned for six weeks, when, on one very cold day, in moving things it was set in the window next the glass, and presently it became a mass of crystals. These did not melt when returned to the warmer air of the laboratory. A new preparation was at once commenced as above.

dissolves a small portion of the crystals, leaving the remainder as this preparation III of the pentiodide. Preparation II of the methyl pentiodide was obtained from the mother liquor of the methyl octaiodide by evaporation and redissolving the crystals in alcohol.

The preparations of the pyridine methyl diiodide in I and II were from solutions quite different from each other from the beginning, but in both cases they were from later crops of crystals following the addition of free pyridine to solution of the other two materials. The final crystals of I were washed in a very little cold alcohol, and then dried over sulphuric acid for ten days. The crystals of II were obtained fine by rapid formation in alcohol surrounded by a freezing mixture.

The preparations of pyridine methyl triiodide in I, II and III were crystallized from the mother liquids of II of the corresponding diiodide. II of the triiodide was itself recrystallized several times. I and III were in more compact crystals of slower formation. But IV was the result of a different method throughout, following the addition of iodine solution to the methyl normal iodide, using proportions intended for the diiodide. The final crystals were by a single recrystallization of the first crop. It was dried between filter papers over sulphuric acid.

The preparations of pyridine methyl octaiodide (provisionally so termed) were instituted by adding eleven grams of the normal iodide dissolved in a little alcohol, to fifty-five grams of iodine in as little alcohol as possible, both solutions being hot. The greenish black oil-like mass separated at once. The decanted solution was cooled, and other portions of the oil obtained. Below  $0^{\circ}\text{C}$ . the oil crystallized well. I was crystallized from solution in alcohol at low temperature. II was crystallized from alcohol by spontaneous evaporation out of doors in cool weather. The final crystals of each were dried between filter papers, and kept in the vault at about  $12^{\circ}\text{C}$ .

Pyridine ethyl triiodide was obtained following the addition of alcoholic solution of the normal iodide to alcoholic solution of iodine. The first product, chiefly higher iodides, appeared in an oil-like precipitate, and this, after decanting the alcoholic liquid, was dissolved in hot alcohol, and the solution kept for six

hours at  $-4^{\circ}$  C. without obtaining crystallization. Afterward crystals were obtained but without success in drying them. Moist with the oil they gave figures a little too low for the tetraiodide. Repeating the entire operation, but not decanting the oil, the entire mixture was exposed to low temperature as before, and the oil solidified in a mass of fine crystals better than before, but these melted below  $10^{\circ}$  C., and the attempt to obtain a pure high periodide had to be deferred. That the oil, which is stable when dried and has no odor of iodine, contains high iodine additive combination was shown by its analysis, giving figures midway between hexiodide and heptiodide. Now the alcoholic liquid decanted from the oil in the first operation, on cooling below  $0^{\circ}$  C., gave an excellent crop of crystals. These, dried for several days over sulphuric acid, at about  $21^{\circ}$  C., constitute the preparation described under the name pyridine ethyl triiodide.

PERIODIDES OF THE AMINE AND OF THE TERTIARY  
AMMONIUM BASE.

1. *Pyridine Tetraiodide*,  $C_5H_4N.I_4$ .—Adding to pyridine an alcoholic solution of iodine until the precipitate ceased to form, thereby leaving a slight excess of iodine, there was obtained a bulky crystalline precipitate of a green color, not of a red color as reported by Dafert.<sup>1</sup> This precipitate was filtered out, drained, washed with alcohol, and drained dry, all under the filter pump, then dried between filters over sulphuric acid for several days. It was found soluble in alcohol, ether, chloroform, and less readily in benzene. It was recrystallized from benzene in I, from chloroform in II, and from alcohol in III. In each result the crystals were dark lustrous green. Those of III were in button-like aggregations of fine needles, the whole about half an inch in diameter. From each solution the crystals showed the same melting-point,  $85^{\circ}$  C. The alcoholic mother-liquor on evaporation gave a crop of very small dark-green crystals IV of the same melting-point. All these crystals gave off perceptible traces of iodine on standing in a glass-stoppered bottle, being very perceptibly less stable than the crystal preparations of the various pyridine *quaternary* base periodides already described. This instability may be the cause of the slight deficiency of iodine found in analysis, the resulting figures being as follows:

<sup>1</sup> 1883, *Monatsh. Chem.*, 4, 509.

	Calculated for $C_5H_5N.I_4$	I.	Found. II.	III.	IV.
Iodine total, by silver iodide .....	86.49	85.72	85.94	85.63	85.48
Iodine by titration with thiosulphate		85.05	84.79	85.73	85.63

This periodide, therefore, contains no iodine firmly bound as in all normal iodides, none that is not promptly taken up by thiosulphate. In this constitutional feature it is a periodide sharply unlike all the pyridine alkyl periodides known, and unlike the pyridine hydrogen pentiodide found by Dafert,<sup>1</sup> and further described below as examined by us. A superbromide of pyridine was obtained, in 1882, by Grimaux,<sup>2</sup> who writes for it the formula,  $(C_5H_5NBr_5)HBr$ . He found it not very stable; in analysis he made but one estimation of bromine, that by silver bromide; and he found the compound reduced by hydrogen sulphide to pyridine hydrobromide and hydrobromic acid. The triethylphosphine tetraiodide,  $P(C_2H_5)_3I_4$ , *inferred* by Masson and Kirkland in 1889,<sup>3</sup> is of the same type as our pyridine tetraiodide. Treated with hydrogen sulphide half its iodine entered into phosphonium normal iodide, and half into hydriodic acid.

Several months before the preparation of pyridine tetraiodide as above given, a product was obtained in another way which puzzled us at the time, but which we now recognize as this last-formed pyridine tetraiodide. It was obtained in the first crystalline precipitate after adding free pyridine to the solution of methyl iodide and iodine, in the second way for making the methyl periodides. The mother-liquor of the precipitate gave us the methyl diiodide, preparation I of that product. The precipitate itself crystallized from a chloroform solution, gave very dark green short needles, melting at  $84.5^\circ C.$ , and soluble in ether and in benzene. The total iodine was found as 86.32 per cent (the average of four results, lowest 86.22, highest 86.50). At that time a satisfactory titration for iodine was not obtained

<sup>1</sup> F. W. Dafert, 1883, *Monatsh. Chem.*, 4, 508. Dafert says, p. 509, "In alkoholischer und in wässriger Lösung des Pyridins erzeugt Iod in Alkohol, respective in Iodjodkaliumlösung ebenfalls unter gewissen Umständen eine Fällung. Eben so bei Anwendung von Schwefelkohlenstoff. Das dabei erhaltene Präparat ist roth gefärbt und jedenfalls mit dem obigen Superiodid *nicht* identisch. Eine weitere Untersuchung wird wohl näheres ergeben." We have not been able to find a further publication by Dafert upon this compound.

<sup>2</sup> E. Grimaux, *Compt. rend.*, 95, 87; *Bull. Soc. Chim.*, 38, 127.

<sup>3</sup> *J. Chem. Soc.*, 55, 139.



on account of the solvent, but without any solvent one slow titration resulted in 85.82 per cent., indicating the absence of normal iodine, when the preparation was put aside for later inquiry. It appears, therefore, that when free pyridine is added to methyl iodide and iodine, in alcoholic solution of each, some periodide of pyridine without methyl is formed in the first precipitate, notwithstanding the extreme avidity with which pyridine unites directly with methyl iodide.

2. *The Pyridine Hydrogen Pentiodide of Dafert.*<sup>1</sup>—This was obtained, following the plan given by that author, in crystals such as described by him, melting at about 85° C. (Dafert 89° C.) In analysis it gave 88.03 per cent. of total iodine, and 70.20 per cent. of iodine by titration (calculation for  $C_5H_5N.HI.I_4$ , total iodine 88.77 per cent., and superiodine 71.02 per cent.). For the titration the periodide was dissolved in alcohol, the end reaction was sharp, and the result conclusive as to the fundamental difference between the two compounds, one of which we believe to be a periodide of  $C_5H_5NH$ , and the other of  $C_5H_5N$ .

A hydrogen periodide of pyridine, therefore, like alkyl ammonium periodides in general, includes for each atom of nitrogen (in the molecule whatever its magnitude) just one atom of iodine which is left united to the nitrogen after the action of reducing agents of sufficient strength. On the contrary the periodides of pyridine not having ammonium hydrogen or alkyl contain no iodine left by such reducing agents in union with the base, as we say, no iodine firmly bound. Various forms of these two types may be represented as follows:

- (1)  $R_4NI.I_n$ , quarternary alkyl ammonium periodides.  
 $(R'''N)RI.I_n$ , quarternary pyridine periodides.  
 $(R'''N)HI.I_n$ , pyridine hydrogen periodide.
- (2)  $(R'''N).I_n$ , pyridine (amine) periodide.  
 $(R'''N)Br_4HBr$ , a superhalide (Grimaux).  
 $R_4PI_n.I_n$ , inferred by Masson and Kirkland.

#### ESTIMATIONS OF THE IODINE OF PERIODIDES.

1. The total iodine is obtained by precipitation as silver iodide, weighing this on filters to be described later.

<sup>1</sup> 1883: *Monatsh. Chem.*, 4, 508.

The sample is weighed, from a weighing bottle, by difference into a No. 2 beaker. About twenty cc. of a saturated solution of sulphurous acid is added, then a slight excess of silver nitrate solution (used of known strength). The mixture is heated on the water-bath for about an hour, breaking the crystals of periodide if necessary with a flat end of a glass rod, then acidulated strongly, using twenty to thirty cc. of nitric acid, (sp. gr. 1.20), and heated one to two hours or until the precipitate is of a uniform light straw color and the liquid perfectly clear. The precipitate is then put upon the prepared funnel of ascertained weight and washed, first with five per cent. nitric acid and then with hot water, using the pump throughout. The funnels are small sized "carbon tubes," the bottom loosely fitted with a glass plug or shoulder, on which is a layer of cracked glass, twelve to twenty mm. thick, made from beakers and sieved to pass a ten-mesh but not a twenty-mesh. After this is washed level, under pressure of the filter-pump, a layer of acid-washed asbestos is floated over it, and the whole dried at 130° to 150° C. for about two hours or for constant weight. Weighing is done with duplicate funnels, suspending them with an aluminum loop.

The washed silver iodide in the funnel is dried, with its duplicate (also wetted), for two hours at 130° to 150° C., or until weight is constant. A set of about thirty of the funnels have been in hand, and when all have been used, the asbestos layer and precipitate are carefully removed, and a fresh asbestos layer floated on, all which can be done for the set in about two hours.

Two to four parallel estimations have been made, and the average taken. The agreement of the estimations is fairly shown in these figures, quoted from the results: 86.69, 86.79, 86.84, 86.66; 72.45, 72.08, 72.45 ; 86.65, 86.29.

2. The iodine in excess of that for a normal iodide, that is, the iodine responding to reducing agents, has been estimated volumetrically by thiosulphate, using a solution of which one cc. equals 0.010 of iodine. To make this solution, "C. P. sodium thiosulphate" is recrystallized small by stirring while the solution cools. The volumetric solution is standardized by standard solution of potassium dichromate, which in turn is checked with one standardized with "chemically pure" iron wire. The dichro-

mate is purified by fusing a chemically pure article and pouring upon a tile. The factor of the thiosulphate solution is taken every two or three days. The periodide analyzed is weighed by difference, from a weighing bottle into a No. 3 beaker, taking 0.150 to 0.600 gram. Of alcohol from ten to fifteen cc. are added. All the periodides so far obtained are soluble in cold alcohol, but with much difference in the readiness and abundance of this solubility, and this property governs the speed of the estimation. The crystals can be broken under a flat end of a rod, and if not readily soluble, the titration is commenced before solution is completed, keeping down the excess of the iodine-like color. At the end starch can be used as an indicator, but after practice this is not necessary, as the extinction of the iodine-like color can be read to within one drop of the thiosulphate. The burettes had been calibrated and were used with a table of corrections. Other solvents have been tried but alcohol proves far the best for the crystals in titration. Two to four titrations have been made and the average given in each estimation. The agreement of the titrations is represented by a few quotations: of the pyridine methyl diiodide, 37.01, 37.24, 36.48, 37.17; pyridine methyl triiodide, 78.55, 78.84.

UNIVERSITY OF MICHIGAN.

### ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND ARSENIC.<sup>1</sup>

BY LAUNCELOT ANDREWS.

Received September 9, 1895.

THE experiments described in the present paper were carried out under my direction during the last winter by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch,<sup>2</sup> and of Jannasch and Schmitt<sup>3</sup> on the same subject. All experiments referred to here, relate to the analysis of an alloy containing in round numbers eighty per cent. lead, thirteen per cent. antimony, seven per cent. tin. The exact composition of this metal will be given later.

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *Ber. d. chem. Ges.* 27, 3335.

<sup>3</sup> *Ztschr. anal. Chem.*, 9, 274.

## FIRST METHOD.

The attempt was made to drive off all tin and antimony as chlorides according to Drown. To this end one gram of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to  $200^{\circ}\text{C}$ . The latter was moistened with about four cc. fuming hydrochloric acid and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilizing all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as follows: Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing ten cc. of nitric acid of 1.50 sp. gr., and then through a combustion tube of large diameter, thirty cm. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion tube is covered with an asbestos tent and heated by means of an Argand burner to  $210^{\circ}\text{C}$ . The amount of the alloy used in each experiment was a half gram, and in two hours, during which time the operation required no attention whatever, the separation was complete and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion tube with hydrochloric acid. The small amount of arsenic present was easily separated from

the contents of the receiver by distillation according to Gooch and Phelps.<sup>1</sup> After the removal of the arsenic, tin and antimony were separated by Carnot's method,<sup>2</sup> which was found to be excellent.<sup>3</sup>

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

## ANALYTICAL RESULTS.

	I. Gram.	II. Gram.	III. Per cent.	IV. Per cent.
Alloy taken .....	0.5000	0.5000	....	....
Lead sulphate.....	0.5849	0.5853	....	....
Lead found.....	0.3988	0.3991	79.75	79.82
Antimony trisulphide...	0.0925	0.0925	....	....
Antimony found .....	0.0661	0.0661	13.21	13.21
Stannic oxide .....	0.0434	0.0437	....	....
Tin found .....	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total.....			99.92	100.05

## SECOND METHOD.

It has been observed that when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidizing action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was

<sup>1</sup> *Ztschr. anal. Chem.*, 7, 123.

<sup>2</sup> *Ztschr. anal. Chem.*, 33, 650.

<sup>3</sup> In this method, the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

confirmed by an experiment in which potassium iodide took the place of the bromide.

One gram of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide, (about one gram) was entirely disintegrated. The antimony remained undissolved as a dark gray powder. It was filtered from the boiling solution through a Gooch filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent. too high if the metal is weighed directly.

## ANALYTICAL RESULTS.

	I.	II.
Metal taken.....	1.0000	1.0000 grams.
Antimony weighed direct....	0.1385	0.1375
Antimony trisulphide.....	0.1827	0.1833
Antimony calculated.....	0.1305	0.1310
Antimony .....	13.05	13.10 Per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II gives the figures obtained by the first method above described. Column III those of the second method. Column IV the mean of all of the results.

## SUMMARY.

	I. Per cent.	II. Per cent.	III. Per cent.	Mean. Per cent.
Arsenic.....	0.13- 0.12	0.12	0.14- 0.13	0.128
Antimony.....	13.13-13.15	13.21-13.21	13.05-13.10	13.14
Tin .....	6.83- 6.84	6.84- 6.88	.....	6.85
Lead.....	79.87-79.95	79.75-79.82	.....	79.85
Total.....	99.97			

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500° which are difficult to secure with certainty by means of a Bunsen or even in some cases by the ordinary forms of air-bath. The

device consists simply of an ordinary Argand gas burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at  $400^{\circ}$ , but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, etc., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate.

### THE DETERMINATION OF GRAPHITE IN PIG-IRON.<sup>1</sup>

BY P. W. SHIMER.

Received September 16, 1895.

THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic-carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidizing action of the solvent. But, experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydrochloric acid are due to the presence, in the graphitic residue, of titanium carbide,<sup>2</sup>

<sup>1</sup> To be read at the Atlanta meeting of the American Institute of Mining Engineers.

<sup>2</sup> See *Trans. Am. Inst. Min. Eng.*, 15, 455.

and possibly of other insoluble carbides, the carbon of which is, of course, included with the graphite in the final determination. In the nitric acid method, the titanium carbide is easily dissolved, and its carbon appears with the combined carbon, when the latter is determined by difference between graphitic and total carbon.

The method by solution in dilute sulphuric acid is open to the same objection as that by solution in hydrochloric acid; for titanium carbide is insoluble in sulphuric acid, and, I may add, it is also unattacked by hydrofluoric acid, and by a boiling solution of caustic potash.

The following is an analysis of a pig-iron unusually high in titanium:

	Per cent.
Silicon .....	3.650
Phosphorus .....	1.145
Sulphur.....	0.010
Manganese .....	0.226
Graphitic carbon.....	3.206
Combined carbon.....	0.128
Titanium .....	0.399
Iron (by difference) .....	91.236
	<hr/>
	100.000

The total carbon in this iron was determined by dissolving in an acidified solution of double chloride of copper and potassium, and subsequent combustion. The graphite was determined by solution in dilute nitric acid and combustion. A determination of graphite, made by solution in hydrochloric acid and combustion, gave 3.327 per cent. of graphite, a result 0.121 per cent. higher than that obtained by the nitric acid method. The amount of carbon combined as titanium carbide (TiC) with 0.399 per cent. of titanium is 0.1 per cent., which counts as graphite in the determination by solution in hydrochloric acid. The results may be set down as follows:

	Per cent.
Total carbon.....	3.334
Graphite by nitric acid solution.....	3.206
Graphite by hydrochloric acid solution.....	3.327

The error in the hydrochloric acid method falls heavily upon



the resultant estimate of combined carbon, which is determined by difference, as appears below :

	Per cent
Combined carbon, when graphite is determined by nitric acid	0.128
“ “ “ “ hydrochloric “	0.007

An experiment was made to determine the action of boiling nitric acid (1.20 sp. gr.) on the graphite from this iron. A sample of two grams was dissolved in hydrochloric acid (1.10 sp. gr.). After washing the graphitic residue with water, it was boiled gently for one hour with nitric acid (1.20 sp. gr.), with the addition of a little water from time to time, to keep up the bulk of the solution. The graphite as thus determined, was 3.203 per cent. against 3.206 per cent., by direct solution in nitric acid, showing that the treatment, for one hour, with boiling nitric acid, had dissolved out the titanium carbide without having attacked the graphite. The graphite in this high silicon iron, however, was coarse and perhaps unusually resistant to the oxidizing action of nitric acid. It is proposed to make similar experiments on the graphite from a variety of pig-irons.

The 0.128 per cent. of combined carbon is made up as follows :

	Per cent.
Carbon combined with 0.399 per cent. titanium as TiC .....	0.100
Combined carbon soluble in hydrochloric acid (probably combined with iron and manganese) .....	0.007
Carbon possibly existing as insoluble carbide other than titanium carbide.....	0.021

A careful mechanical separation of a few grams of titanium carbide was made from several pounds of this iron by use of the long, slightly inclined glass plane described in the paper before the Institute referred to above.

Besides titanium and carbon in this separation, there is some vanadium, apparently also existing as an insoluble carbide, which would account for a part of the above 0.021 per cent. of combined carbon. This investigation is, however, still under way.

The writer has never encountered a pig-iron free from tita-

nium, the amount found varying usually from 0.05 to 0.40 per cent. In irons with a coarsely crystalline fracture, the cubical crystals of titanium carbide may always be found when carefully looked for. The conclusion seems to be fair that the hydrochloric acid method includes, with the graphite determined by it, the carbon existing as insoluble titanium carbide. With pig-irons containing from 0.05 to 0.40 per cent. of titanium, the graphite so determined will be from 0.013 to 0.100 per cent. too high, while the combined carbon will be correspondingly low.

It follows that more light would be thrown upon the condition of the carbon in pig-iron by making three determinations: *viz.*, one of total carbon, one of the carbon insoluble in hydrochloric acid, and one of graphite by the nitric acid method. We would thus have determinations of graphitic carbon; carbon combined with iron and manganese, soluble in hydrochloric acid; and carbon combined as carbides insoluble in hydrochloric acid. In high-silicon, low-sulphur titanic irons, the insoluble form of combined carbon exceeds the carbon existing as soluble carbides of iron and manganese. It is important to know how the carbon is combined. One-tenth per cent. of carbon combined with titanium in the condition of disseminated microscopic crystals, probably has no effect on the hardness of pig-iron; while the same amount of carbon, combined with iron and manganese, would have an appreciable hardening effect. Practically, therefore, it may be desirable to have the carbon existing as carbides insoluble in hydrochloric acid appear with the graphite as determined by the hydrochloric acid method, although the actual graphite can be determined only by solution in nitric acid. At all events it is essential to know by what method graphite has been determined, in order to draw conclusions from determinations of graphitic and combined carbon in pig-iron.

## ON THE COMPOSITION OF PELAGINE.

BY A. B. GRIFFITH AND CHARLES PLATT.

Received October 7, 1895.

THE chemical composition and constitution of the violet pigment of Pelagia (one of the Medusae) has been established by us, as follows: By treatment with hot alcohol and ether the pigment and fats are dissolved and the solution, after filtration, is evaporated carefully to dryness. The residue is treated with a solution of sodium hydroxide and the pigment then rapidly extracted by means of carbon disulphide. Upon the spontaneous evaporation of the solvent, the violet pigment is obtained as an amorphous residue.

Analysis of this pigment gave the following results:

I.	Substance employed .....	0.2058	gram.
	Carbon dioxide .....	0.47325	"
	Water .....	0.0810	"
II.	Substance employed .....	0.4605	"
	Nitrogen .....	15.15	cc.
	Barometric reading .....	742.	mm.
	Temperature .....	15°	

Reduced to percentages and calculating the formula the following results are obtained:

	I.	II.	Calculated for $C_{30}H_{17}NO_7$ .
Carbon .....	62.71	....	62.66
Hydrogen .....	4.38	....	4.43
Nitrogen .....	....	3.75	3.66
Oxygen .....	....	....	29.24

Analysis, then, would indicate the formula  $C_{30}H_{17}NO_7$ . Pelagine is soluble in alcohol, in ether, and in acetic acid; it is insoluble in water, but it is very soluble in carbon disulphide. Solutions of the pigment are decolorized by exposure to light and, on spectroscopic examination, do not yield characteristic absorption bands. It has, apparently, no respiratory function and probably belongs to the same order of pigments as tetronerythrin,<sup>1</sup> rhodopsin, etc.; in other words, pelagine is probably a lipochrome or a nitrogenous derivative of that class. In certain respects it may be said to resemble melaine, the pigment of Sepia, investigated by Girod, Variot, and Desfosses.<sup>2</sup>

<sup>1</sup> *Compt. rend.*, 93, 1029.

<sup>2</sup> *Compt. rend.*, 93, 97.

## ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

BY H. L. WELLS AND W. L. MITCHELL.

Received July 22, 1895.

THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago, F. Pisani<sup>1</sup> stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet color no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyze a large number of titanic iron ores and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of

<sup>1</sup> *Compt. rend.*, 59, 289.

the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidized under such circumstances.

Marignac,<sup>1</sup> with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time, but the feature of his process which is interesting in the present connection is that he reduced the titanic acid by means of a long rod of pure zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac by using sulphuric acid solutions and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:

Five grams of very finely pulverized ore are placed in a rather large beaker covered with a watch-glass and treated with about 100 cc. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and when no further action is apparent about fifty cc. of a mixture of equal volumes of concentrated sulphuric acid and water are added and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 cc. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a liter flask. With many titanic ores this operation will have dissolved everything except silicious matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium

<sup>1</sup> *Ztschr. anal. Chem.*, 7, 112.

disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the liter flask. Filtration may be omitted here, or in the case of the original solution, provided that the silicious matter is not to be weighed.

The liquid in the liter flask is diluted to the mark and mixed, and four portions of 200 cc. each, representing one gram of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 cc. capacity, and the other two into ordinary flasks of 350 cc. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about twenty-five cc. of concentrated sulphuric acid are added, then in each case three or four rods of chemically pure zinc, about fifty mm. long and six or seven mm. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them

near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty minutes, then, without interrupting the boiling, a glass tube, so bent that it extends fifty mm. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid ( $\text{TiO}_2$ ).

When a fifty cc. burette is used, the most convenient strength for the permanganate solution is when one cc. is equal to about 0.014 grams of metallic iron, corresponding to seven and nine-tenths grams of potassium permanganate per liter.

It is customary in this laboratory to standardize permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated because they have an equal effect upon the standardization and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 cc. flask is half filled with sulphuric acid, (the strong acid diluted with about eight volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and after the air has been expelled, about six-tenths gram of the purest iron wire, representing nearly the average amount of iron in one gram of an ore, is dropped in and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidizing agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride,  $K_2TiF_6$ , was recrystallized twice from water and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid and the amount of zinc used. The following table gives the results obtained in grams :

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	—0.0090
0.6425	0.1225	0.1285	—0.0060
0.7778	0.1524	0.1555	—0.0031
0.6793	0.1308	0.1358	—0.0050
0.8226	0.1607	0.1645	—0.0038
1.0956	0.2107	0.2191	—0.0084
0.4451	0.0848	0.0890	—0.0042
0.6359	0.1215	0.1271	—0.0056
0.9004	0.1715	0.1800	—0.0085
0.4634	0.0882	0.0926	—0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished, by recrystallizing it, and it is exceedingly difficult to obtain any titanium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method



would be increased by adding one-twentieth or one-thirtieth to the amount of titanio acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titaniofluoride taken	Titanium Found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter.

SHEFFIELD SCIENTIFIC SCHOOL,  
NEW HAVEN, CONN.

### ARSENIC IN GLYCEROL.<sup>1</sup>

BY G. E. BARTON.

Received September 9, 1895.

IN following up the literature of glycerol I find that the first to note the presence of arsenic in the medicinal article was Jahns,<sup>2</sup> but he apparently did not investigate the subject thoroughly.

E. Ritsert<sup>3</sup> was the next to take the subject up. He showed the presence of arsenic in seven samples of medicinal glycerol, by the following test, which he says shows 0.001 mg. in one cc. while the Marsh test shows only 0.01 mg. in one cc. One cc. of glycerol is placed in a small measuring cylinder and to this one cc. of water is added, together with fifteen drops of hydrochloric acid and 0.6 gram zinc. The top of the cylinder is covered with filter-paper, moistened with a 1 : 1 silver nitrate solution or saturated mercuric chloride solution, and a yellow stain is obtained on the paper if arsenic is present. Ritsert also states that ammoniacal silver nitrate solution is a good reagent for arsenious acid and that the arsenious acid present probably

<sup>1</sup> Read at the Springfield Meeting.

<sup>2</sup> Pharm. Ztg., 1888, 652.

<sup>3</sup> Pharm. Ztg., 1888, 715, and 1889, 104, 360 and 625.

explains the difference in the indications given by litmus and phenolphthalein as observed by him. He gives as the probable source of the arsenic found, the sulphuric acid used in the course of manufacture. Issue is taken with G. B. Smith,<sup>1</sup> who states that glycerol itself reduces silver nitrate, and hence ammonio-silver nitrate can not be used to detect arsenic.

An abstract of an article by G. Vulpius<sup>2</sup> gives the cost of an article free from arsenic as ten per cent. more than the current price.

L. Siebold<sup>3</sup> on "Arsenic in Glycerol," finds from one in 4000 to one in 6000 parts of arsenious acid in glycerol used for perfuming and medicinal purposes, and in one case one part in 2500 parts. All glycerols free from arsenic were traced to one process described as that "by which as a rule glycerol used for dispensing purposes is understood to be made." He ascribes the presence of arsenic in some cases to the solution of the arsenic present in the glass of the bottle, but this has never been confirmed and hardly seems probable.

Dr. Benno Jaffé<sup>4</sup> attacks the ammonio silver nitrate test which he claims to be of no value as it does not give constant results, either for arsenic or acrolein and similar bodies.

J. Luttké,<sup>5</sup> after an elaborate examination of twenty-one samples confirms Jaffé's conclusions and points out as among the disturbing causes, chlorides and organic acids.

There can be no doubt of the presence of arsenic in some glycerol, but I have found no one except Siebold who has attempted to give any idea of the quantity, and while he does not give the method used in obtaining the results stated, I infer from the text that, using either silver nitrate or mercuric chloride to absorb the hydrogen arsenide, he has compared the depth of color obtained with that given by known quantities of arsenious acid. A few experiments led me to think that this cannot be a very accurate method at best, so I set about to apply the method given by Sanger, for the estimation of arsenic in wall paper,<sup>6</sup> which

<sup>1</sup> Ned. Tijdschr. v. Pharm., 1889, 143.

<sup>2</sup> Apoth. Zeit., 1889, 4, 439; *J. Soc. Chem. Ind.*, 8, 639.

<sup>3</sup> Pharm. J. Trans. [3], 20, 205.

<sup>4</sup> Chem. Ztg., 1890, 14, 1493.

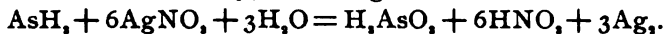
<sup>5</sup> Apoth. Ztg., 1891, 6, 263.

<sup>6</sup> Proc. Amer. Acad., 26, 24.

consists of comparing the mirrors obtained in a modified form of the Marsh apparatus with those prepared from known quantities of arsenious oxide in solution as sodium arsenite.

The apparatus as described by Sanger consists of a constant hydrogen generator, filled with chemically pure sulphuric acid and zinc, a smaller reduction flask having a thistle tube for introducing acid and solutions to be treated and which of course contains a small amount of chemically pure acid and zinc, a drying tube containing calcium chloride, and finally a reduction tube in which the mirror is obtained.

The cost of using chemically pure acid and zinc in the constant hydrogen generator would of course be great, and the first point I turned my attention to was a method for purifying the hydrogen generated by impure acid and zinc so that the constant generator could be run at a reasonable cost. I found that by passing the hydrogen through silver nitrate solution, the arsenic was removed entirely, according to the well-known reaction:



Another improvement in the apparatus as I used it was the substitution of a small separating funnel for the thistle tube in the reduction flask. This prevented the escape of any gas at that point while the former arrangement allowed a variable quantity to escape.

The apparatus as finally used in this work, consisted of a constant hydrogen generator, using impure acid and zinc, a wash bottle containing silver nitrate solution, a wash bottle containing water to remove any traces of silver nitrate solution which the gas might carry mechanically and which would otherwise hold back some of the arsenic in the reduction flask, a reduction flask, with separating funnel as before described, a drying tube containing calcium chloride, and finally the reduction tube.

The efficiency of the silver nitrate solution was proven by running over one hundred hours without obtaining a mirror, whereas a mirror could be obtained in from five to ten minutes from the same hydrogen not passed through silver nitrate. Using the ordinary acid and zinc of the laboratory, I found an amount of silver nitrate solution representing one gram of the salt prevented the formation of a mirror for over two hundred hours.

The mode of operating did not differ essentially from that described by Sanger. The apparatus was first filled with hydrogen, the reduction flask containing at this time only the pure zinc, of which about three grams were used. The jet at the end of the reduction tube was then lit and the tube heated at the proper place, after which a little sulphuric acid was introduced into the reduction flask and the action allowed to go on for a few minutes to prove the purity of the reagents. The solution to be treated was then added and washed in by more acid, or water where the glycerol was added directly to the flask.

The acid used was about one to eight and by slightly varying these proportions it was found possible to get along without cooling the flask. No two samples of zinc were found to contain the same amount of carbon or at least to dissolve with the same rapidity so that a careful adjustment of the acid is necessary for each lot and as large an amount as possible should be granulated at one time. It is also necessary to have standard mirrors made at different speeds to counterbalance the slight differences which are unavoidable.

The calcium chloride tube should be carefully looked after in order that the gas may be perfectly dry. I have found it best to ignite the article furnished by the makers before using. It is also a good plan to attach the bellows and blow through it a few moments after filling, to remove any slight amount of dust that might otherwise be carried into the reduction tube.

The glass used for the reduction tube should be of the hardest obtainable. I have found great variations in different pieces of the same lot. It would be of advantage if glass were carefully selected, and if necessary carefully tested, could be quoted by dealers, as otherwise a large amount of tubing is accumulated too hard for ordinary work but not hard enough for this purpose. Great care should always be taken to get tubes uniform at the point of deposition and in spite of this it was found necessary to have several mirrors of each grade.

A small white mirror was found to form beyond the arsenic mirror in those tubes representing small amounts but in those obtained from larger amounts either wholly or partly coinciding. In the latter case the arsenic mirror took on a totally different

color, the characteristic brown of the pure arsenic mirror becoming black. This mirror was without doubt in some cases partly due to moisture, and showed minute drops when examined under a lens. It also seemed to be less with the harder glasses. After having used fresh calcium chloride and the hardest glass obtainable, the only resource is in having standard mirrors representing all possible variations.

Another trouble was found to be the deposition of the arsenic in two mirrors entirely apart. This Gooch and Moseley<sup>1</sup> suggest to be due to the formation of two allotropic forms of arsenic by the too high heating of the reduction tube. They avoid this by enclosing the reduction tube in an iron or nickel jacket. Here again several mirrors of each standard amount are a remedy.

Having obtained a sufficient number of standard mirrors eight samples of glycerol, such as is ordinarily sold by the druggists of this city were procured. Six represented the best American makers and two were imported.

Five grams of each sample were treated with five cc. of a mixture of thirty parts sulphuric acid and one part nitric acid and the mixture heated carefully with constant stirring till a dry charred mass giving off sulphur dioxide was obtained. This was then allowed to cool and about ten cc. of water added and then the mass again heated till sulphur dioxide was given off. After cooling about fifteen cc. of water was added and the mixture boiled vigorously to expel sulphur dioxide. The liquid was then filtered off and water added as before, boiled and again filtered. This was repeated twice to insure the complete extraction of the arsenic from the charred mass. The solution thus obtained was added to the reduction flask and the usual process carried out. Five of the eight samples showed arsenic in variable amounts.

To prove that arsenic, if present, would be shown by this course of manipulation, five grams of glycerol showing no arsenic were weighed out and one cc. of an arsenic solution added. This mixture was treated exactly as the other samples had been and no arsenic mirror obtained. From this and the comparison

<sup>1</sup> Am. J. Sci., 48, 294.

of these mirrors with those obtained by other processes, I concluded that some, at least of the samples contain, or are decomposed into something capable of holding black arsenic. This leads to the query: What is the effect of the combined glycerol present in the toxicological examination for arsenic? May not the trouble with the glycerol be due to a decomposition product which would also be formed in the supposed case? I have not had time to investigate this important point.

Five grams of the same glycerol used in the previous experiment were then added direct to the reduction flask after diluting with water and arsenic in small quantities was obtained. One cc. of the arsenic solution was then added to the glycerol and, after diluting, the reduction carried out at once as in the previous experiment and an amount of arsenic equal to that in the one cc. of solution and five grams of glycerol, obtained. After trying several plans this method was finally chosen as both the quickest and most accurate.

The following quantities of arsenious oxide ( $\text{As}_2\text{O}_3$ ) were obtained in the eight samples:

No.		No.	
1	..... trace.	5	..... faint trace.
2	..... 0.08 mg.	6	..... trace.
3	..... faint trace.	7	..... 0.004 mg.
4	..... none.	8	..... 0.003 mg.

To prove that the mirrors obtained were due to arsenic and nothing else, mirrors were heated gently and moist hydrogen sulphide passed through them. In this manner part of the arsenic was changed to the yellow sulphide. Some of the gas from the reduction flask was passed into silver nitrate solution and a black precipitate of metallic silver obtained. On carefully neutralizing with ammonium hydroxide a yellow precipitate of silver arsenite, soluble in excess, and also in nitric acid was obtained. The nitric acid solution was precipitated with hydrochloric acid, a clean copper wire added and the solution warmed. A grey coating formed on the copper. Blank experiments showed the reagents to be pure.

From the above there can be no doubt but that arsenic was present in the glycerols examined.

The method mentioned by several authors, namely, diluting

the glycerol with an equal volume of water, adding hydrochloric acid and then metallic zinc, and obtaining a yellow coloration on a filter-paper moistened with either silver nitrate solution (1 : 1) or saturated mercuric chloride solution was tried. A twenty-five cc. measuring cylinder was used and the paper fastened tightly over the mouth, the gas escaping at the nose. In this manner using the silver nitrate solution the test was found to be about five times as delicate as the Marsh test used, and a trace of arsenic was found in sample No. 4, which had shown none in the Marsh test. The coloration was not permanent enough, owing to the action of light and other causes to be compared with standards made with permanent coloring-matters. The test with mercuric chloride, carried out in the same way, was not quite as delicate as the Marsh test. It would hardly be possible by comparing with standards to make this a quantitative method as accurate as the Sanger-Berzelius-Marsh test. It is to be noted that sample No. 2, which showed the largest amount, contained 0.08 arsenious oxide or one part in 62500, while Siebold reports as much as one part in 2500 in one case. Seventy mg. is the smallest dose known to have produced death according to Tanner<sup>1</sup> which would be equivalent to the amount in over four liters of glycerol No. 2, or to 150 cc. of Siebold's worst sample. Although arsenic is slowly eliminated from the system, still it would be quite possible by the indiscriminate use of sample No. 2, for some time, to accumulate enough in the system to cause death. Certainly the above figures are worthy of note by persons using glycerol for medicinal purposes.

So-called C. P. glycerol is often recovered from the waste products of the soap manufactories, and in this case the presence of arsenic is accounted for as follows: Starting with arsenical oil of vitriol, the arsenic is changed in the hydrochloric acid still to the chloride, which distils over with the acid. On neutralizing the spent lyes with hydrochloric acid the arsenic remains in the solution and is repeatedly distilled over with the glycerol.

In this connection I may say that I found no hydrochloric acid in this laboratory free from arsenic as shown by the yellow stain in the silver nitrate test, but had no trouble in preparing such

<sup>1</sup> Memoranda of Poisons, p. 69.

an article from chemically pure sulphuric acid which I had proven to contain no arsenic.

In conclusion I take pleasure in acknowledging my deep indebtedness to Dr. Charles E. Munroe for his many suggestions.

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

## THE OCCURRENCE OF TRIMETHYLENE GLYCOL AS A BY-PRODUCT IN THE GLYCEROL MANUFACTURE.<sup>1</sup>

BY ARTHUR A. NOYES AND WILLARD H. WATKINS.

Received September 9, 1895.

**D**URING the past winter our attention was called to an unusual difficulty experienced by one of the soap-making firms in the neighborhood of Boston in obtaining their glycerol of the required commercial gravity. The information furnished in regard to it indicated the presence in the glycerol of some uncommon impurity, and a considerable quantity of the "light stuff" having been generously placed at our disposal by the soap company, we were enabled to investigate it. It was submitted to fractional distillation, first at diminished and then at ordinary pressure, and a liquid boiling between  $214^{\circ}$  and  $217^{\circ}$  at 760 mm. pressure was thus separated from it. This liquid was found to have a specific gravity of 1.056 at  $77^{\circ}$ , and gave the following results on analysis:

0.2293 gram substance gave 0.3998 gram carbon dioxide and 0.2158 gram water.

	Found.	Calculated for $C_3H_8O_3$ .
Carbon .....	47.52	47.37
Hydrogen .....	10.46	10.53

The substance is therefore trimethylene glycol, which has a boiling-point of  $214^{\circ}$  and a specific gravity at  $77^{\circ}$  of 1.0526. The isomeric propylene glycol boils at  $188^{\circ}$ – $189^{\circ}$  and has a specific gravity of 1.0403 at  $77^{\circ}$ . The "light stuff" contained a very considerable proportion, about thirty-eight per cent. of glycol.

The origin of the glycol is a matter of considerable interest. There is little doubt that it was produced by fermentation of the

<sup>1</sup> Read at the springfield meeting.



glycerol. For it has already been shown by Freund<sup>1</sup> that trimethylene glycol is, in fact, one of the principal fermentation products of that substance. It is moreover highly probable that the glycol was present in the fat before saponification by the alkali, as the fermentation can hardly have taken place in the soap lye, both on account of its saline character, and on account of the short time intervening between the saponification and the recovery of the glycerol. It had probably been produced in the fat by spontaneous saponification and subsequent fermentation of the glycerol.<sup>2</sup> Refuse house fat formed a considerable part of the soap stock.

The presence of the glycol in glycerol used for making nitroglycerol might be a source of danger, since it reacts with nitric acid with explosive violence. Its presence would be detected in the usual examination by a low specific gravity accompanied by a high oxidation equivalent as shown by the bichromate titration.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.

## THE EVOLUTION METHOD FOR THE DETERMINATION OF SULPHUR IN WHITE CAST-IRON.<sup>3</sup>

BY FRANCIS C. PHILLIPS.

Received September 9, 1895.

THIS method is based upon the assumption that when iron is dissolved in an acid any sulphur that may occur in the iron unites with the escaping hydrogen, forming hydrogen sulphide. In the usual mode of conducting the process the impure hydrogen evolved is led into a suitable absorbent and the sulphur finally determined, either by oxidation and precipitation as barium sulphate, or by a volumetric method. In applying the process Fresenius<sup>4</sup> directs that the iron be dissolved in *dilute* hydrochloric acid. Von Reis<sup>5</sup> and Blair<sup>6</sup> concur in this recommendation, as does also Dudley in

<sup>1</sup> Monatsh. Chem., 2, 638.

<sup>2</sup> Mr. E. Twitchell of Cincinnati informs us that he has found the glycol present in considerable quantity in the "tank liquor" separating from the fat before saponification.

<sup>3</sup> Read at the Springfield meeting.

<sup>4</sup> Quant. Analyse, 1877, 428.

<sup>5</sup> Stahl-elsen, 1894, 963.

<sup>6</sup> Chemical analysis of Iron, p. 54.

the published directions for the determination of sulphur in cast-iron, issued by the Pennsylvania Railroad Company.

For the absorption of the hydrogen sulphide various reagents have been recommended. Johnson<sup>1</sup> proposed the use of a bromine solution. Blair absorbs the hydrogen sulphide in an alkaline solution of lead acetate, oxidizes the resulting lead sulphide, and precipitates the sulphuric acid as barium sulphate. According to the usage at many iron works the gases are led into an ammoniacal cadmium chloride solution which is afterwards acidulated and the sulphur determined volumetrically by standard iodine. In order to complete the expulsion of the hydrogen sulphide from the solution of ferrous chloride a stream of carbon dioxide has been generally employed. Blair uses for this purpose a current of hydrogen, while Dudley states that neither gas has any advantages over air used in a slow stream. In iron-works laboratories it is a generally recognized fact that in the use of the evolution method for certain cast-irons, notably those containing a high percentage of combined carbon, an error is liable to occur, and in cases where great accuracy is required the aqua regia method is usually preferred.

It is common to find that during the solution of cast-iron in an acid there is produced a considerable quantity of strong smelling gaseous hydrocarbons. The interior surface of the flask becomes coated with minute drops of an oily liquid which adheres to the glass and is not miscible with water. There can be little doubt that the loss of sulphur which often results in its determination by the evolution method is dependent largely upon the formation of these organic compounds during the solution of the iron.

It is common to find that the white irons dissolve in acid leaving a nearly white silicious residue of a somewhat flocculent character. This residue contains a varying amount of sulphur, which is insufficient, however, to account for the low results sometimes obtained in the determination.

It has been attempted to explain the error on the hypothesis that sulphur exists in iron in more than one modification, that that portion of the sulphur which occurs in the ordinary form

<sup>1</sup> *Ztschr. anal. Chem.*, 1874.

passes readily into hydrogen sulphide on its elimination from the iron by the action of the hydrochloric acid, while another portion existing in some unknown modification, is not converted into hydrogen sulphide, but remains passively in the residue and is thus lost in the determination.

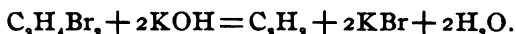
Such an assumption involves a difficulty. It is not usually considered necessary in order to explain the chemical changes undergone by the elements of a compound to suppose that the atoms of carbon, hydrogen or sulphur exist in the compound in forms different from those in which we know them in other compounds. Of the six hydrogen atoms in alcohol one differs from the others as to its behavior towards oxidizing agents. The supposition that there are two allotropic forms of hydrogen in alcohol would hardly be accepted, however, for it is commonly believed to be the mode of linking of the atoms rather than the occurrence of the elements in allotropic forms in the compound that determines the nature of chemical changes. The fact that a portion only of the sulphur in white cast-iron is liberated as hydrogen sulphide by an acid suggests that the molecule of cast-iron does not contain all its sulphur linked in the same manner. In the present paper I have described some experiments undertaken in order to study the reactions of the evolution method more fully. For the purpose in view a white iron containing 0.17 per cent. of sulphur, as found by the aqua regia method was used.

*Experiment 1.*—Four grams of this iron were dissolved in hydrochloric acid of 1.12 sp. gr. As the process of solution became retarded the acid was heated gradually to the boiling-point. The escaping gas was led into a solution of bromine. A small quantity of a heavy oil collected in the bromine solution. This oil was decanted, introduced into a platinum boat and burnt in a porcelain tube in a current of nitrous oxide gas. The gas escaping from the tube was led into bromine water, which on treatment with barium chloride in the usual way yielded a precipitate of barium sulphate, showing that the original oil had contained sulphur.

*Experiment 2.*—The oil collected in an experiment similar to the preceding was digested with concentrated nitric acid. The

mixture, contained in a glass-stoppered bottle, was kept at a temperature of  $100^{\circ}\text{C}$ . for two hours. On one evaporation to dryness, re-solution of the residue in water, and addition of barium chloride no precipitation occurred. The solution was then evaporated again to dryness with addition of some barium nitrate, and the residue heated to redness. On re-solution in water a precipitate of barium sulphate appeared. This experiment showed that the oil contained sulphur but in a form not easily oxidizable directly to sulphuric acid by bromine water or concentrated nitric acid. The fact that a precipitate of barium sulphate was not obtained by mere evaporation with strong nitric acid, but was quickly produced on ignition of the evaporated residue and re-solution in water, indicated the possible presence of a sulphur ether of the type  $(\text{CH}_2)_n\text{S}$ .

*Experiment 3.*—That the oil condensed in the bromine flask was not a pure sulphur compound was evident from the following experiment: A few drops of the oil were warmed in a flask with an alcoholic solution of potassium hydroxide. The escaping gas was found to yield a red precipitate in an ammoniacal solution of cuprous chloride, indicating acetylene. From this it seemed probable that the oil found in the bromine solution consisted mainly of ethylene dibromide, which on treatment with the alcoholic potash had yielded acetylene by the reaction



*Experiment 4.*—The flask which had been used for a sulphur determination by the evolution method, and which exhibited minute oil drops on its inner sides, was rinsed with alcohol and with chloroform. The combined liquids were evaporated in a platinum boat in which a minute quantity of a residue was left. On strongly heating in nitrous oxide and passing the products into bromine water a precipitate of barium sulphate was obtained after the usual treatment with barium chloride.

*Experiment 5.*—The silicious residue left from the solution of the iron in hydrochloric acid in the determination of sulphur by the evolution method was found on fusion with alkaline carbonate and nitrate to yield a small quantity of barium sulphate when treated in the usual manner for the determination of sul-

phuric acid. It seemed still to be of importance to ascertain whether the sulphur in this residue existed as a metallic sulphide or as an organic compound. The possibility of the presence of free sulphur seemed to be excluded, inasmuch as air had been expelled from the flask during the solution of the iron by a stream of carbon dioxide. Accordingly, the silicious residue from a sulphur determination was dried at a gentle heat and extracted after the fashion of an ordinary fat extraction process by boiling alcohol and afterwards by boiling chloroform. The extract, on evaporation, left a trace of a yellow oil. This oil, on being burnt in nitrous oxide, gave indications of the presence of sulphur when tested in the manner already described.

The silicious residue, after extracting with alcohol and chloroform, was found, on fusion with alkaline carbonate and separation of the silica, not to contain sulphur. From this it appeared that the silicious residue contained an organic sulphur compound, but did not contain a metallic sulphide.

The acid solution of ferrous chloride left in the evolution flask was filtered, agitated with a few cc. of chloroform. The chloroform on evaporation, ignition of the residue in nitrous oxide, and the usual treatment, was shown to contain sulphur.

The following determinations were made in the manner indicated. The percentages of sulphur are based upon the weight of the iron dissolved.

	Per cent.
1. Sulphur from oil collected in bromine solution....	0.008
2. Sulphur obtained from alcohol and chloroform rinsings of flask.....	0.010
3. Sulphur extracted from silicious residue.....	0.013
4. Sulphur obtained by <i>fusion</i> of silicious residue after extracting by alcohol and chloroform.....	0.000
5. Sulphur obtained by agitation of the filtered ferrous chloride solution with chloroform, representing therefore organic sulphur compounds held in solution .....	0.009
<b>Total.....</b>	<b>0.040</b>

This total represents sulphur occurring in difficultly volatile organic compounds and does not include that which is evolved in more volatile compounds. It is not impossible that a loss by

volatization occurred in evaporating the chloroform extracts preparatory to combustion in nitrous oxide. It seemed very desirable to learn more of the nature of these organic sulphur compounds and accordingly the following experiment was tried with a larger quantity of iron.

*Experiment 6.* One thousand grams of the same white iron as had been used in the preceding experiments were treated in small portions at a time with hydrochloric acid of 1.15 sp. gr. until the solution was complete. To hasten the process, as the action of the acid became slow, the flask was gently warmed. The escaping gas was passed, first, through a solution of lead acetate supersaturated with sodium hydroxide, and secondly, through a solution of mercuric chloride in alcohol.

#### I. THE ALKALINE LEAD ACETATE SOLUTION.

In addition to the deposit of lead sulphide which formed in the lead solution, a yellow flocculent precipitate appeared, soluble on shaking in the alkaline fluid. The solution, decanted from the lead sulphide, was slightly acidulated and warmed. The gas produced was found to yield the following reactions with the solutions named:

Ammoniacal cadmium chloride yielded a white flocculent precipitate.

Palladium chloride yielded a cinnamon colored precipitate.

Platinum chloride yielded a yellowish brown precipitate.

Ammoniacal silver nitrate yielded a pale yellow precipitate.

These reactions indicated the presence of a mercaptan. To study the subject more fully the yellow precipitate, produced in a solution of silver nitrate containing an excess of sodium acetate, was subjected to a partial analysis with the following results:

Silver.	Sulphur.	Silver.	Sulphur.
Found.		Calculated for silver mercaptide.	
69.40	20.54	69.63	20.68

From the data so obtained it appears that methyl hydrosulphide was contained in the gas evolved during the solution of the iron in the hydrochloric acid.

#### 2. THE ALCOHOLIC SOLUTION OF MERCURIC CHLORIDE.

This was found to contain a small quantity of a white precipi-

tate which was partly soluble on warming. After cooling again the solution yielded transparent colorless crystals recognized under the microscope as having the form of crystals of the compound  $(\text{CH}_3)_2\text{SHgCl}$ , which results when methyl sulphide is added to a solution of mercuric chloride. Upon boiling the aqueous solution of the precipitate in the mercuric chloride solution and leading the vapors into palladium chloride solution, orange crystals were obtained which under the microscope were not distinguishable from the compound formed when palladium chloride and methyl sulphide are brought together. The precipitates formed in the solutions of mercuric chloride and palladium chloride being somewhat soluble, the quantity obtained was insufficient for analysis. It is however very probable that methyl sulphide  $(\text{CH}_3)_2\text{S}$  occurred among the gases evolved during the solution of the iron.

It seems important that in the evolution method of sulphur determination the possibility of the presence of these and kindred sulphur compounds should be taken into account. Two modes of procedure suggest themselves for the recovery of that portion of the sulphur which is liable to be lost in the determination.

I. By direct oxidation to sulphuric acid.

II. By conversion into hydrogen sulphide followed by oxidation to sulphuric acid.

#### I. DIRECT OXIDATION OF ORGANIC SULPHUR COMPOUNDS.

The action of concentrated nitric acid, potassium permanganate and other energetic oxidizing agents in solution tends merely to convert methyl sulphide into its oxides  $(\text{CH}_3)_2\text{SO}$  and  $(\text{CH}_3)_2\text{SO}_2$ . Bromine enters into direct union forming  $(\text{CH}_3)_2\text{SBr}_2$ .

Under strongly oxidizing influences methyl hydrosulphide merely yields methylsulphonic acid, an acid which is well known to form a soluble and stable barium salt. Hence while it is a characteristic property of hydrogen sulphide to undergo oxidation to sulphuric acid readily, it is equally characteristic of these organic sulphur compounds and their homologues not to change easily into sulphuric acid even under apparently favorable conditions.

It seemed possible that by direct combustion of the gases the complete oxidation of the sulphur to sulphuric acid might be effected.

A great many experiments have been tried in this direction of which the following is a summary.

As the gases are not evolved in sufficient quantity during the solution of the iron to burn steadily from a jet, it was found necessary to conduct through the evolution flask a current of some combustible gas in order to maintain a more constant flame. For this purpose carbon monoxide was used. The gas was burned from a platinum jet in a glass globe through which a current of moist nitrous oxide was caused to flow. Nitrous oxide was used rather than air or oxygen for the reason that during the combustion of any gas in it nitrogen dioxide is continually formed in considerable quantity. The conditions are therefore highly favorable to the oxidation of any sulphur dioxide produced from the flame of the burning gas, and the complete condensation of the resulting sulphuric acid.

The results were not satisfactory for two reasons :

1. It was found impossible to prevent the occasional extinguishing of the flame, due to the slight pulsations in the gasstream.
2. It was not possible to expel all of the less volatile hydrocarbon oils from the evolution flask into the combustion globe without boiling the ferrous chloride solution and consequent risk of driving over too much steam which tended to extinguish the flame. These difficulties necessitated the abandonment of the method.

## II. CONVERSION OF ORGANIC SULPHUR COMPOUNDS INTO HYDROGEN SULPHIDE.

The precipitates produced by the mercaptans in solutions of metallic salts, are not easily converted into sulphides. From this statement must be partially excepted the lead, silver and copper compounds which may change slowly into sulphides. The cadmium compound, which is often seen as a white precipitate when in the evolution method ammoniacal cadmium chloride is used as an absorbent, is more stable. The white precipitate gradually changes into yellow cadmium sulphide, especially on exposure to light.



The process adopted by Blair—absorption in alkaline lead solution—no doubt possesses an advantage on account of the possible change of the lead compound into lead sulphide, as it in this way may affect the recovery of a portion of the lost sulphur. The compounds of the sulphur ethers of the type  $\text{HgCl}_2(\text{CH}_3)_2\text{S}$  are still less prone to change into metallic sulphides under the conditions imposed by the method.

*Experiment 7.*—The vapor of methyl sulphide largely diluted with carbon dioxide was passed through a red hot porcelain tube. By this treatment the sulphur compound was shown to be readily convertible into hydrogen sulphide, undergoing, however, an intermediate transformation into methyl hydrosulphide,  $\text{CH}_3\text{SH}$ , a gas which is easily recognized by its reactions with various metallic salts in solution.

Based upon the results of these experiments the following modification of the evolution method was tried:

The iron was dissolved in hydrochloric acid of 1.12 sp. gr. added slowly while a stream of carbon dioxide was being transmitted through the flask. Heat was applied as soon as the action became retarded. The escaping gas was led through a porcelain combustion tube heated to dull redness. The porcelain tube contained a roll of platinum foil eight inches long. The delivery tube from the evolution flask was pushed far enough into the porcelain tube to permit any liquid which might distil over to drop into the hot platinum roll. A slow stream of carbon dioxide was passed continuously through the evolution flask and heated porcelain tube. The solution of the ferrous chloride was finally heated to gentle boiling and kept boiling until the oily drops which usually coat the sides of the flask were carried away. This required two hour's boiling or two and one-half hours for the entire process. Inasmuch as organic compounds of high boiling-point are undoubtedly formed, this long-continued boiling is especially important. As an absorbent, bromine dissolved in dilute hydrochloric acid was used. After passing a nitrogen flask containing the bromine solution the gas was conducted to the bottom of an eight liter bottle containing a little of the same bromine solution. Experiments have shown that the use of this large bottle is necessary to the complete con-

densation of the sulphuric acid. The platinum foil used in the porcelain tube is not essential but protects the porcelain tube from risk of fracture from the dropping of the liquid upon its heated inner surface. Mica may be used instead of platinum but is rapidly corroded by the hot acid vapors. The sulphur was determined by weighing as barium sulphate.

In the following table column II contains the results of some determinations of sulphur by the method described.

Column I contains results obtained by the same method except that no heated tube was used.

Column III contains results obtained by the aqua regia method as described by Blair.<sup>1</sup>

The irons used for the determinations were selected on account of their high percentage of sulphur.

Evolution method. Per cent.	Evolution method. Gases passed through a heated tube. Per cent.	Aqua regia method of Blair. Per cent.
<b>IRON A.</b>		
0.059	0.096	0.101
0.046	0.095	0.098
0.050	0.104	0.096
0.050	0.104	0.099
0.054	0.099	0.100
0.055	0.100	0.102
....	0.092	0.102
....	0.105	0.104
....	0.098	....
....	0.101	....
Mean 0.052	0.099	0.100
<b>IRON B.</b>		
0.100	0.183	0.173
0.101	0.178	0.170
0.087	0.175	0.168
0.099	0.181	0.170
0.092	0.177	0.174
0.084	0.188	0.171
Mean 0.094	0.180	0.171

In conclusion, I have to thank Messrs. F. B. Smith and H. C. Beggs for the very great care they have taken in carrying out the determinations by the method described.

<sup>1</sup> Chemical Analysis of Iron, p. 57.

## ON THE VOLUMETRIC DETERMINATION OF LEAD.

BY ALLERTON S. CUSHMAN AND J. HAYES-CAMPBELL.

Received September 26, 1895.

FRESENIUS in the last edition of his Quantitative Analysis commenting on the volumetric determination of lead, says : " Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz,<sup>1</sup> briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator owing to the yellow color of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle<sup>2</sup> modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow color of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow color gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavor to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardized solution of ammonio ferrous sulphate, using potassium ferricyanide as an outside indicator under exactly the same conditions observed in standardizing bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardized against a weighed amount of pure dried ammonio ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then

<sup>1</sup> *Dingl. poly. Jour.*, 169, 284.

<sup>2</sup> *Ztschr. anal. Chem.*, 1880, 306.

weighed out and dissolved in a liter of water with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a siphon tube and pinchcock so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio ferrous sulphate solution takes place very slowly, while as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well mixed sample of a crystallized galena containing only a little silica as impurity was first analyzed by the method of Rose as given in Fresenius, Quantitative Analysis. The lead is precipitated as the sulphide, with the proper precautions, the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained :

No.	Weight taken. Grams.	Weight lead sulphide. Grams.	Lead sulphide. Per cent.	Lead. Per cent.
1	2.0000	1.9870	99.35	86.08
2	2.0000	1.9856	99.28	86.00
3	1.9988	1.9856	99.35	86.06

The next series of results were obtained by the method of Albert H. Low.<sup>1</sup> Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried and weighed. By this method the following results were obtained :

No.	Weight taken. Grams.	Weight lead. Grams.	Lead. Per cent.
1	0.5000	0.4341	86.82
2	0.5013	0.4311	86.00
3	0.4972	0.4313	86.64
4	0.5025	0.4371	86.98
5	0.5019	0.4351	86.25
6	0.5223	0.4540	86.92

<sup>1</sup>*J. Anal. Appl. Chem.*, 6, 12.

These figures show a general tendency to high results which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's<sup>1</sup> modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands and the percentages found were invariably low. As the method did not present any advantage over others either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows: About one gram of finely pulverized ore is digested in a casserole or evaporating dish with fifteen cc. of a mixture of two parts nitric and one part sulphuric acid until decomposition is complete. Ten cc. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with ten cc. of dilute sulphuric acid (1-10) and then add gradually forty cc. of water. Heat to boiling, filter and wash by decantation with dilute sulphuric acid (1-10) getting as little of the lead sulphate on the filter as possible. To the residue in the dish add twenty cc. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow color. Allow to settle for a few minutes then filter, under pressure if possible, wash a few times and titrate the filtrate against the standard ammonio ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be

<sup>1</sup>J. Anal. Appl. Chem., 6, 11.

free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution, the acid is neutralized with an excess of ammonia and then made acid with acetic acid; this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:

No.	Weight taken. Grams.	Calculated weight lead found. Grams.	Lead per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
6	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.

CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY,  
ST. LOUIS, MO.

## REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID.<sup>1</sup>

BY CHAS. BASKERVILLE.

Received September 9, 1895.

ANDREWS<sup>2</sup> in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary pro-

<sup>1</sup> Read at the Springfield meeting.

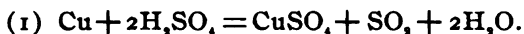
<sup>2</sup> Chem. News, 70, 152.; Iowa Acad. of Sciences, Proc. p. 4.

duct. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction so simply treated in most text-books.

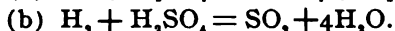
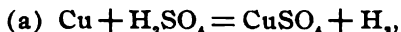
When my work was completed, in verifying my references I chanced on Pickering's<sup>1</sup> work on the same subject which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Prof. Pickering. My observations concerning the primary reactions were not the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

Primary:



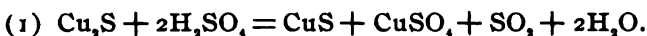
This may be regarded as taking place in two steps:



Still no hydrogen could be detected in the gas given off.



Secondary:



The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated C. P. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide

<sup>1</sup> J. Lond. Chem. Soc. Trans., 1878, p. 112.

and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experiment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper as sulphate was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue treating with carbon disulphide and the loss in weight taken as sulphur.

*Primary Reactions.*—My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures ( $0^{\circ}$ – $270^{\circ}$  C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occurred. The proportion of the material following the second equation increased from  $0^{\circ}$  to  $100^{\circ}$  C., and then decreased to  $270^{\circ}$  C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under  $100^{\circ}$  C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from  $100^{\circ}$  to  $130^{\circ}$  C. as may be seen from the table. The proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at  $270^{\circ}$  C. and lasts for only a few seconds.



No.	Temperature of reaction.	Copper used.	Copper as sulphate.	Copper as sulphide.	Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°-10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°-30°	1.3379	1.3260	0.0121	....	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0.1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°-80°	0.0760	0.0730	0.0035	....	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°-130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°-160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°-190°	1.1375	1.1200	0.0930	....	12.0 : 1
13	200°-220°	1.5450	1.4518	0.0932	1.0904	16.0 : 1
14	220°-230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°-260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	....	None.	....	....

Berzelius<sup>1</sup> noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel<sup>2</sup> found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming copper sulphide and oxide, the latter being dissolved in the acid.

Maumené<sup>3</sup> claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides,  $\text{CuO} \cdot 2\text{Cu}_2\text{S}$  or  $\text{Cu}_2\text{S}_2\text{O}_3$ ,  $\text{CuO} \cdot 2\text{CuS}$  or  $\text{Cu}_2\text{S}_2\text{O}_3$ , and  $\text{CuO} \cdot \text{CuS}$  or  $\text{Cu}_2\text{SO}$ .

In my analyses, as also in Pickering's, the sum of the percent-

<sup>1</sup> *Traité de chimie*, 4, 324.

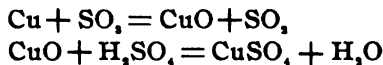
<sup>2</sup> *Journ. de Pharm.* 20, 13, 1834.

<sup>3</sup> *Ann. Chim. Phys.*, 1846, 3rd Series, 18, 311; *Traité de chimie générale*, Pelouze et Fremy, 2nd Ed., I, 388.

ages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated  $\text{CuO}_2\text{Cu}_2\text{S}$ . I shall speak of that apparent exception further on.

Calvert and Johnson<sup>1</sup> performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from  $130^\circ$  to  $150^\circ$  C. They noted the formation of the sub-sulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.<sup>2</sup> There was evidently something very wrong in their observations, for they failed to note any action below  $130^\circ$  C. Barruel in 1834 had noted that action took place at the temperature of the air. I have noted the action at  $0^\circ$  C.

According to Andrews



are the correct formulas,  $\text{SO}_2$  existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at  $0^\circ$  C. Besides this the undissolved residue is not the oxide at all, as he says it is, but invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I have learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.	Calculated for $\text{Cu}_2\text{S}$ .
Sulphur.....	20.44	20.14
Copper.....	79.56 (by difference)	79.86
	<u>100.00</u>	<u>100.00</u>

In the first of the two primary reactions,



<sup>1</sup> J. Chem. Soc., 19, 438, 1866.

<sup>2</sup> Pickering proved this impossible. The amount of sulphide produced was not increased by adding sulphur direct to the experiment.

it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved. Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as sulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula



shows that relation between the two compounds of copper.<sup>1</sup>

*Secondary Reactions.*—The secondary reactions depend upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150° C when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59.<sup>2</sup>

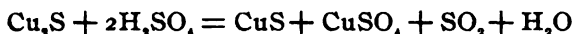
<sup>1</sup> Pickering states (*loc. cit.*, p 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2 : 2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

<sup>2</sup> Watts (vol. II, p. 41, 1875, Ed.) notes this complete decomposition.

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur .....	32.36	33.59

The formula,



explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur .....	19.71	20.138

The formula



shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1.  $\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$
2.  $\text{CuS} + 2\text{H}_2\text{SO}_4 = \text{S} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons :

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.
2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.
3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.
4. If flowers of sulphur be heated with concentrated sulphuric

acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

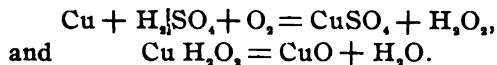
## COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated  $\text{CuO} \cdot 2\text{Cu}_2\text{S}$  in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to  $250^\circ \text{C}$ . in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis :

	Found.	Calculated for $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ .
Sulphur .....	16.16	16.15
Oxygen .....	3.54	4.03
Copper .....	undetermined	79.82

Schuster<sup>1</sup> found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube<sup>2</sup> noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for  $\text{SO}_4$  and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being :



I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen peroxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering<sup>3</sup> sug-

<sup>1</sup> *Proc. Roy. Soc.*, 55, 84; *Ber. d. chem. Ges.*, 28, 219.

<sup>2</sup> *Ber. d. chem. Ges.*, 18, 1887-1890.

<sup>3</sup> *Loc. cit.*, p. 138.

gests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

UNIVERSITY OF NORTH CAROLINA.

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### NEW BOOKS.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY. Volume I, Soils. Cloth, 8 vo., pp. 607, figures, 93. Easton: Chemical Publishing Co. 1894. Price, \$3.75.

This first bound volume includes the first eight parts of the compendious work now in process of publication.

In attempting to meet the wants alike of analysts, teachers, and students of agricultural chemistry, the author has undertaken a most difficult task. The needs of the several classes of readers are widely different, often distinctly opposite.

Beyond doubt, each of the classes named has need of a thoroughly modern treatise upon this subject. There is extant no satisfactory systematic introduction through the general principles of analysis to the special methods applicable to agricultural materials; the student is ordinarily compelled to the study of many methods, in the illustration of general principles and for the acquirement of facility in manipulation, that are not directly required in his future work, and which might often be happily substituted by methods which are of immediate use. Again, there is no English work on agricultural analysis—except of the most incomplete scope—which is at all modern; nor does any work upon the subject in any language cover the methods developed in America during the past ten years. On the other side, the Proceedings of the Association of Official Agricultural Chemists state the American official methods most briefly, for the guidance of analysts presumably acquainted with the methods in general, and more or less familiar with the reasons for the several specifications, and, therefore, without explanatory comment; nor has this Association undertaken, as yet, to cover all of the large field involved. Even assuming a degree of linguistic attainment altogether beyond that of the average student, and of

many a practicing analyst, the foreign treatises upon the subject are often so brief as to mislead the student and to be useless even to the practicing analyst. The opening for a treatise of the design outlined by Professor Wiley is therefore wide.

The perspective of the volume will serve quite well, perhaps, to elucidate the author's treatment of his subject in its salient features; of 607 pages, over one-tenth is devoted to a brief study of the materials to be analyzed, and their origin; one-twentieth is given to the sampling of the soil; one-seventh to the physical properties of the soil, including their estimation; one-sixth to mechanical and mineralogical analysis; one-thirtieth to the determination of the gases of the soil; the remaining half of the volume deals with the chemical analysis of the soil, including soil waters.

In no other treatise of this kind are the relations of the analytical method to the nature of the problem it is used to solve, so fully dwelt upon; and in no other similar treatise do the physical and mineralogical properties receive a treatment so fully in accord with their importance.

The style is clear and compact. In his selection of methods no attempt has been made by the author to limit those described to the number found useful in a single laboratory only, but general experience has rather been consulted. Especial stress is laid upon American methods because the reader will chiefly use these methods, and because other treatises so frequently ignore them; yet no other treatise gives nearly as full discussion even to the Continental official methods, and the judicial impartiality of the author is highly praiseworthy. The very recent literature has been drawn upon for material, and the wealth of reference will be especially appreciated by the teacher and analyst; this volume alone contains 348 listed references to original papers.

This work is furthermore noteworthy as being probably the first important chemical treatise to rigidly follow the American Association for the Advancement of Science revision of chemical orthography. The practice of beginning with a lower-case type all proper names used in the text to designate methods is an innovation less certain to be followed. The figures are well selected and apposite.

The publishers are to be congratulated on the beautiful typography of the volume, its good press-work, and its freedom from printer's errors.

Judging of this work by the first volume it may be said, briefly, that it is the most modern, the most complete and the very best treatise upon the subject of agricultural analysis, and that it meets more largely than any other book on the subject, the needs of the teacher, the student, and the working analyst. It is not, of course, a text-book of agricultural chemical analysis, nor a hand-book of the laboratory, but it should find its place upon the reference tables of all laboratories. Nor is its usefulness confined to the analyst of agricultural products alone, for every general analyst will find in its pages a great mass of material, superbly arranged, to which he could daily refer with direct advantage to his work.

WILLIAM FREAR.

A HAND-BOOK OF INDUSTRIAL ORGANIC CHEMISTRY. BY SAMUEL P. SADTLER, PH.D., F.C.S. Second revised and enlarged edition. 8 vo. pp. 537. Philadelphia: J. B. Lippincott & Co. 1895. Price, cloth \$5.00, sheep \$6.00.

The hundreds of manufacturers of chemical products in this and other countries who are struggling with the puzzling problems of daily practice and the vexatious details so essential to commercial success, eagerly watch for and greedily accept everything which may possibly clear up difficulties or offer suggestions, and such works as this of Dr. Sadtler's find the heartiest of welcomes waiting for them. It is not surprising, therefore, that this work from so excellent authority should soon be out of print and that a second edition should be needed to meet the current demand.

Limited in volume, and, therefore, in detail, works of this class serve two important purposes: First, they furnish teachers in compact and reliable form for presentation to their students, ample description of the principles and processes used in the chemical industries. Second, they furnish manufacturers, working in more or less empirical ways, knowledge of the fundamental principles of the processes they employ, or general principles of methods other than their own but attaining the same end, possibly with greater economy both of time and means.

In the second instance they meet only partially the prevailing



demand. Manufacturers are desirous, it is true, of becoming acquainted with the experience of others even in other branches of industry; but the difficulties they meet are frequently, if not generally, as much mechanical as chemical, and better and more effective forms of apparatus as well as general reactions are needed. Furthermore, profits in manufacture depend in these days largely upon the utilization of the waste products, and the practical operation of many processes are dependent upon the retention or destruction of wastes, noxious or undesirable. Methods and apparatus are wanted for properly caring for these important factors of the industrial problems.

In the work before us Dr. Sadtler has succinctly set forth the progress attained to date in the industries discussed and in a large measure has met the demands described. Perfection is rare, and doubtless many of us might be able to suggest additions to the several chapters dictated by personal experience; yet with the material offered, together with the bibliography, the references to other and larger works and particularly to the periodical literature, it is questionable if one can find a better time saver in all the range of technical-chemical publications than is provided in this work.

In fourteen chapters, covering 492 pages, the industries most common to this country, at least, are discussed under five general heads, *viz*: Raw materials; Processes of manufacture; Products; Analytical tests and methods; Bibliography and statistics; and in this systematic way the essential facts are presented. Descriptions for empirical work are accompanied by analytical methods for rational control. In addition thereto is an appendix giving conversion tables and tables of physical and chemical constants useful wherever the work may go.

One hundred and twenty-seven most excellent cuts representing machinery and apparatus used in the works or laboratories illustrate the text and fourteen diagrams illustrate the various successive steps in processes of manufacture or analysis. A thoroughly complete index makes reference most convenient and will charm those who have suffered the vexation incident to the use of books not similarly provided.

WILLIAM McMURTRIE.

## BOOKS RECEIVED:

On the Densities of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights. By Edward W. Morley, Ph.D. City of Washington, published by the Smithsonian Institution, 1895. 4°. xi, 117 pp. Price \$1.00.

*From Smithsonian Contributions to Knowledge, Vol. XXIX. (Number 980.)*

The Scientific Foundations of Analytical Chemistry. By Wilhelm Ostwald, Ph.D. Translated by George M'Gowan, Ph.D. New York, published by Macmillan & Co., 1895. 8°. xviii, 207 pp. Price \$1.60.

Organic Chemistry. The Fatty Compounds. By R. Lloyd Whiteley, F.I.C., F.C.S. New York, published by Longmans, Green & Co., 1895. 8°. viii, 291 pp. Price \$1.00.

A Manual of Qualitative Chemical Analysis. By E. P. Harris, Ph.D., LL.D. New edition, revised. Amherst, Mass., printed by Carpenter & Morehouse. 8°. 315 pp. Price \$1.50.

Maps of British Columbia, Nova Scotia, Quebec and Ontario. Ottawa, the Geological Survey of Canada. 1895.

Practical Proofs of Chemical Laws. By Vaughan Cornish, M. Sc. London and New York, published by Longmans, Green & Co., 1895. xii, 92 pp. Price 75 cents.

# THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

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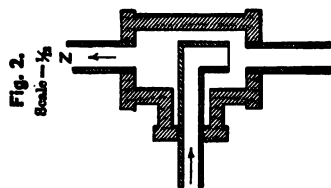
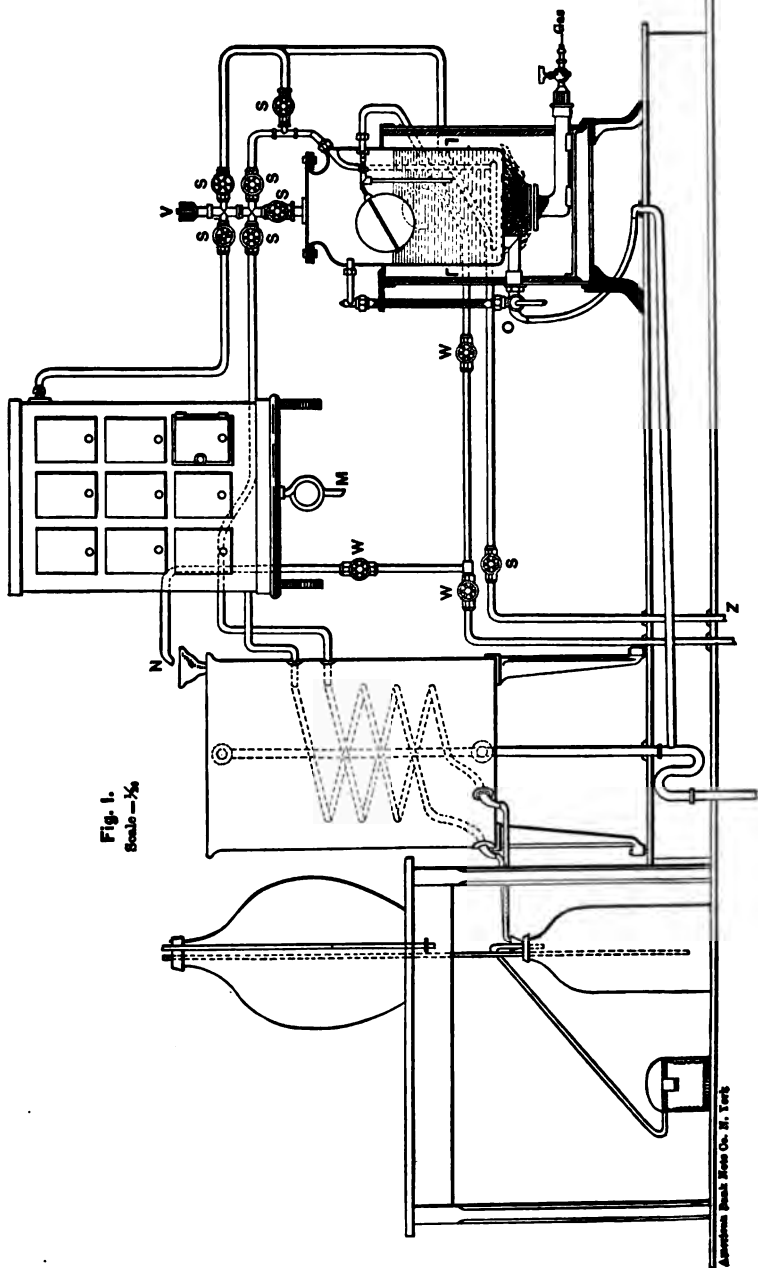
## A CONVENIENT STILL FOR THE LABORATORY.<sup>1</sup>

BY CHARLES E. WAIT.

Received October 14, 1895.

IN the use of the apparatus purchased for the new chemical laboratories of the university, no piece has given us more satisfaction, or has been a greater success, than a new still, which is the subject of this paper. In the designing of this still I had two definite objects in view; one, the utilizing of steam from the large sixty horse-power boiler used in heating the building, and the other, a provision for making distilled water with gas, when steam from the heating-plant was not available. The still is encased in wrought-iron, with a lining of asbestos, and is provided with a float which automatically regulates the flow of water from the supply-pipe. It is a beautiful piece of apparatus, and the workmanship is excellent in every detail. The essential parts of this apparatus will be understood by consulting the accompanying figures, but a few words of explanation may be appropriate. The still has a capacity of seven gallons, and is made of heavy copper, tin-lined. It has a water-gauge showing the height of the water in the still, also an exit for steam, and safety-valve, V; inlet for steam through a coiled perforated block-tin pipe; also an outlet, O, for cleaning out the still; and there is also a heavy disk gas-burner. There is a conveniently-arranged drying-oven and a large condenser, carry-

<sup>1</sup> Read before the American Institute of Mining Engineers.



A CONVENIENT STILL.

ing two block-tin worms, one direct from the still, the other from the oven, both delivering water to a carboy resting on the floor. When steam is taken from the large boiler, provision is made, by an arrangement seen in Fig. 2, located at Z, beneath the floor, to cleanse the steam, before it reaches the still, from the water mechanically carried into the pipes. The water returns to the boiler, while the steam passes to the still. By the arrangement of the steam-valves, S, it is possible to deliver the steam to the empty still, where it is again washed, and may then be passed either to the oven or direct to the condenser or to both. Or the steam from the boiler may be taken direct to the oven or to the condenser or to both. When a small quantity of steam is admitted to the still, most of the distilled water is condensed in the oven and is caught in a copper tin-lined vessel underneath, through the valve, M, a part passing to the condenser and then to the glass vessel, from which it may be forced to the carboy above. When there is no steam in the large boiler gas is used, the water being kept in the still at a constant level by the automatic arrangement before mentioned and seen in the sketch. In this case the steam may be passed to the drying oven or to the condenser direct or to both, as heretofore mentioned. In the case of gas alone, the still has a capacity of about twenty-six gallons of distilled water per day, while with steam from the boiler at a pressure of five pounds, I have made distilled water at the rate of 112 gallons per day. A convenient system of piping has been arranged for supplying water to the still and condenser, to the latter at N, and under control of valves, W, as seen in the sketch. The still and condenser are both connected with the waste, and may be emptied and cleaned when necessary. Other details of this apparatus are shown in the drawings. As I have used this still constantly for a year, and fully appreciate its merits and good points, I have no hesitation in recommending the design to those who may wish a still for the purpose for which this one is used.

## ON THE ESTIMATION OF THE EXTRACTION IN SUGAR HOUSES.<sup>1</sup>

BY M. TRUBEK.

Received September 9, 1895.

ONE of the most important things to be considered in the control of the work in sugar houses is the exact determination of the extraction, that is, the weight of juice obtained from 100 parts of cane. This is calculated in different ways. The raw juice, as it comes from the mill, passes through measured vessels before entering the clarifiers. From the number of the vessels filled or emptied during a certain time, the quantity of juice yielded by a certain weight of cane is determined. When working with dilution, the amount of diluting material has to be subtracted. Or the bagasse, yielded by a certain quantity of cane, is ascertained, and the weight of the cane minus the weight of the bagasse, gives the extraction.

The juice is generally measured directly in the clarifiers, and after making a correction in the volume for the higher temperature the juice has when it reaches the mark in the clarifiers, the per cent. dilution, if there is any; any other quantities added and reintroduced, as lime, syrup washings, etc., are deducted.

The determination of the extraction by this method offers some difficulties. Among others, some of the "quantities reintroduced" are hard to control; the mark in the clarifiers is often not easily seen on account of the foam on top of the juice. Moreover, the person in charge will have to take his figures, as quantity of lime in the different clarifiers, number of clarifiers filled during a certain period, amount of syrup settlings left in the syrup tanks and water used for washing them, etc., from the workmen, who do not give them with the necessary exactness.

It would be of great value, therefore, if a method could be found to determine the extraction from data found in the laboratory only.

In case the juice was not diluted, the extraction can be figured from the fiber in the cane and that in the bagasse.

<sup>1</sup> Read at the Springfield meeting.

In 1865, E. Icery, in an article entitled, "De quelques recherches sur le jus de la canne à sucre et sur les modifications qu'il subit pendant le travail d'extraction à l'île Maurice," admitting the inconveniences in the old method proposed to determine the extraction from the bagasse of the cane under operation; the fiber of the latter is either known or has to be found by analysis. He proceeds as follows:

Two hundred and fifty grams of the bagasse, (care being taken that the latter represent a good average sample), were quickly extracted with luke-warm water and then dried perfectly in a drying stove.

Let  $B$  = weight of the wet bagasse.

"  $B'$  = " " " dry "

"  $C$  = fiber in the cane.

"  $x$  = weight of juice extracted, then  $\frac{100 B'}{C}$  will represent the weight of cane yielding the amount of the wet bagasse  $B$ , and

$$1. \frac{100 B'}{C} - B = x.$$

The extraction  $y$  per 100 parts cane is then found according to

$$2. \frac{100 B'}{C} : x = 100 : y; \quad y = \frac{x C}{B'}.$$

If a determination of the fiber in the cane is not made, the author sets

$C = 10$  for: Belloughet (Java cane).

Diard.

and  $C = 11.5$  " : white or Tahitian.

Batavian.

Guingham (violet ribboned).

Penang.

The equations cited above (1 and 2) become simpler when calculating during the previous procedure the amount of dry bagasse per 100 parts of wet bagasse = fiber per cent. of bagasse.

I<sup>a</sup>.  $F_B : C = 100 : x$ ; II<sup>a</sup>.  $100 - x = E$ , where  $F_B$  = fiber in

<sup>1</sup> *Ann. chim. et. Phys.*, 5, 350-410.

bagasse;  $C$  = fiber in cane;  $x$  = bagasse yielded by 100 parts cane;  $E$  = extraction. Very often, in order to effect a more thorough exhaustion of the sucrose in the cane, water is allowed to run in fine streams on the bagasse, coming from the first set of rollers, and the resulting bagasse contains therefore a certain amount of water not belonging to the cane. In this case I determine the extraction in the following way:

If  $F_{B_1}$  = fiber in diluted bagasse,

$B$  = original bagasse corresponding to 100 parts of diluted bagasse,

$F_C$  = fiber in cane,

$x$  = bagasse resulting from 100 parts of cane,

$E$  = extraction,

we have the following equations:

$$1. \frac{F_{B_1} \cdot 100}{B} : F_C = 100 : x.$$

$$2. 100 - x = E.$$

The unknown figures are  $B$ ,  $x$ , and  $E$ , as  $F_{B_1}$  and  $F_C$  are found by analysis of the cane and its bagasse.

In order to find a third equation we determine the sucrose in the cane, the extracted juice and the resulting diluted bagasse.

Let  $s$  = sucrose in cane,  $s_1$  = sucrose in juice.

$s_{B_1}$  = sucrose in diluted bagasse.

In  $(100 - E)$  bagasse there is left  $\left(s - \frac{E s_1}{100}\right)$  sucrose, or in

$$100 \text{ bagasse } \frac{\left(s - \frac{E s_1}{100}\right) 100}{100 - E}.$$

We have therefore as the third equation:

$$3. \frac{\left(s - \frac{E s_1}{100}\right) 100}{100 - E} = \frac{100}{B} s_{B_1}$$

After eliminating we have

$$E = \frac{a}{2} \pm \sqrt{b + \left(\frac{a}{2}\right)^2}, \text{ where}$$



$$a = \frac{100 F_{B_1} (s + s_1) - 100 s_{B_1} F_C}{s_1 F_{B_1}}$$

$$b = \frac{10000 (F_C s_{B_1} - F_{B_1} s)}{s_1 F_{B_1}}$$

In the equation for  $E$  only the minus sign has to be taken.

Example :

Tons ground..... Nov. 29, 1894.  
1105

Dec. 1, 1894.  
1056

Regular feed on the carrier :

$F_{B_1} = 41.94$  ;  $F_C = 10.64$  ;  $s_1 = 10.95$  ;  $s = 9.785$  ;  $s_{B_1} = 4.80$ .

Substituting in the equation for  $E$  we have

$$E = 89.12 - \sqrt{-7824.05 + 7942.37}$$

$$= 78.25 \text{ per cent.}$$

It is obvious that in order to get good results extreme care must be taken to obtain an average sample of the cane and the bagasse, or the results will not represent the true facts. I will admit that it is not easy to obtain such an average sample and that exact methods for determination of the woody fiber and sucrose in cane and bagasse have not yet been found. In the future I will report more fully on this subject.

CHEMICAL LABORATORY OF RACELAND  
PLANTATION, RACELAND, LA.

## ON SILICIDES OF IRON.

BY G. DE CHALMOT.

Received September 23, 1895.

IRON and silicon readily unite at a high temperature. Silicides of iron of a definite composition have been made by Hahn.<sup>1</sup> He obtained compounds of the formula :  $Fe_3Si$ ,  $FeSi$ , and  $FeSi_2$ .

Since carbon readily reduces silica at the temperature of the electric arc, I expected to obtain silicides of iron with a large percentage of silicon by heating iron with silicon and carbon in an electric furnace. Iron filings, charcoal and sand were used and a silicide was obtained that contained from twenty-three to twenty-seven per cent. of silicon. In order to obtain this compound there must be an excess of sand and carbon. This com-

<sup>1</sup> *Ann. Chem.* (Liebig), 129, 57.

pound is white, crystalline, very hard, brittle and very little magnetic, the more so however if the percentage of silicon decreases. It conducts the electricity very well. In a pure condition it forms sometimes crystals of one cm. long. These crystals have the formula  $\text{Fe}_3\text{Si}_4$ .

	Calculated.		Found.
Silicon.....	25.04	25.17	25.30
Iron .....	74.96	74.75	....

The specific gravity is 6.36. This compound is very resistant against acid oxidizing agents. A sample of the silicide was ground and sieved through a 100 mesh sieve.

Cold aqua regia ( $1\text{HNO}_3 + 3\text{HCl}$ ) dissolved by frequent stirring in two days 9.86 per cent., and in nine days 10.57 per cent. Of a sample of silicide containing 12.85 per cent. of silicon 66.84 per cent. was dissolved by the same reagent in two days. The commercial silicide of iron contained about eleven to thirteen per cent. of silicon, the original silicide contained 24.1 per cent. of silicon, that treated for nine days with aqua regia contained 27.2 per cent., which shows that only iron but no appreciable amount of silicon had been dissolved. The silicide is quite decomposed by hydrofluoric acid and also if it be melted with a mixture of sodium and potassium carbonate to which some potassium nitrate has been added.

Silicides of iron of great purity can be formed from impure materials like coke and river-sand. Iron ore may replace the filings.

I have also prepared in the electric furnace silicides of a higher percentage of silicon, *i. e.*, 29.3, 33.3, and 46.2 per cent.

These silicides seem to be mixtures of the compounds  $\text{Fe}_3\text{Si}_4$  and  $\text{FeSi}_2$ . The latter compound is described by Hahn as metallic greyish crystals.

The material richest in silicon which I obtained contained :

	Calculated for $\text{FeSi}_2$ .	Found.
Silicon .....	50.26	46.22
Iron .....	49.84	53.76

The specific gravity of this material was 4.851. It was very brittle, crystalline, grey and nonmagnetic. Aqua regia dissolved in two days only 0.76 per cent. of the material that had been sieved through a 100 mesh sieve.

## ESTIMATION OF PHOSPHORIC ACID IN SOILS BY DOUBLE PRECIPITATION WITH MOLYBDIC SOLUTION AND TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE WITH STANDARD ALKALI.

By C. B. WILLIAMS.

Received September 30, 1895.

THE accurate estimation of the small quantities of phosphoric acid usually present in the acid extract of soils is a question that has given no small amount of trouble in soil analysis. There seems to be two main difficulties. First, in the precipitation with molybdic solution in the presence of large quantities of iron and aluminum salts, compounds of these latter elements are also often precipitated with the ammonium phosphomolybdate, and are either dissolved by the ammonia wash or remain in the cone of the filter as phosphates, thus giving rise to high or low results, as the case may be, unless special precautions are taken. In the second place very small quantities of phosphoric acid are not precipitated readily by magnesium chloride mixture and usually require long standing to be complete, in which case the precipitate is very liable to contain an excess of magnesia, thus giving rise to higher results.

Some work in the laboratory of the North Carolina Experiment Station upon the samples sent out by Prof. A. M. Peter, reporter of the A. O. A. C. on soils, indicate that these difficulties are readily overcome by the following procedure: The hydrochloric acid extract of the soil is obtained<sup>1</sup> by digesting the soil in acid of 1.115 sp. gr. at the temperature of boiling water and under atmospheric pressure for ten hours. The organic acid (one per cent. citric acid and 0.63 per cent. oxalic acid solutions) extracts<sup>2</sup> are obtained by digestion at laboratory temperature for five hours. Care must be taken to destroy all organic matter in the hydrochloric acid extract as well as in the organic acid extracts. This is done in the former case by adding about one cc. concentrated nitric acid for every three cc. of the portion taken for analysis and evaporating to two or three cc. concentration, and in the latter cases by evaporating the extracts to dryness and igniting with the addition of a small quantity of

<sup>1</sup> U. S. Dept. Agr. Div. Chem., Bul. 43, page 387.

<sup>2</sup> See report of A. O. A. C. Reporter on Soils for 1895.

nitric acid until organic matter is completely destroyed. These residues are now dissolved up to convenient volumes, and portions corresponding to eighteen, twenty or more grams of soil, and portions of the hydrochloric acid extract corresponding to one or more grams of soil (according to the richness in phosphoric acid) are precipitated, after adding about fifteen grams ammonium nitrate, at 40° C., with a large excess of molybdic solution, (thirty cc. is usually enough), let stand four hours, filter and wash with water twice. Now dissolve the precipitate into the beaker used for precipitation with dilute ammonia, wash the filter with dilute nitric acid and add concentrated nitric acid until precipitate begins to re-form; add ten grams ammonium nitrate, digest in water-bath at 65° C., add two cc. strong nitric acid with vigorous stirring, let stand five minutes, add two cc. molybdic solution, let stand eight minutes more and filter, wash and titrate according to volumetric method in this laboratory.<sup>1</sup>

The results presented in the table were obtained in the course of this investigation and show very close agreement with each other on the same solutions.

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID COMPARED WITH  
OFFICIAL GRAVIMETRIC METHOD.

Official gravi- No. of metric sample. method.	Hydrochloric acid solution.		Citric acid solution.		Oxalic acid solution.	
	First solution.	Second solution.	First solution.	Second solution.	First solution.	Second solution.
1	0.4505	0.4170	0.4069	0.0282	0.0290	0.0505
	....	0.4170	0.4069	0.0282	0.0287	0.0505
	....	0.4170	0.4069	0.0282	0.0287	0.0510
	....	0.4170	0.4069	0.0282	0.0287	0.0510
2	0.1720	0.1826	0.1826	0.0119	0.0146	0.0060
	....	0.1775	0.1826	0.0119	0.0146	0.0060
	....	0.1826	0.1928	0.0119	0.0146	0.0065
	....	0.1826	0.1928	0.0122	0.0152	0.0065
3	0.3956	0.3767	0.3867	0.0233	0.0255	0.0475
	....	0.3869	0.3867	0.0233	0.0255	0.0475
	....	0.3869	0.3867	0.0233	0.0255	0.0483
	....	0.3767	0.3818	0.0233	0.0261	0.0483
	....	0.3767	....	....	....	....
	....	0.3818	....	....	....	....
4	0.1932	0.1828	0.1929	0.0157	....	0.0087
	....	0.1878	0.1929	0.0157	....	0.0087
	....	0.1928	0.1929	0.0157	....	0.0087
	....	0.1878	0.1878	0.0162	....	0.0084

N. C. EXPERIMENT STATION, Raleigh, N. C.

<sup>1</sup> See description of volumetric methods in methods of the A. O. A. C. for 1895.

## ON THE USE OF ORGANIC BASES IN THE PREPARATION OF BARIUM AND CALCIUM FERROCYANIDES.

BY PERCY H. WALKER.

Received October 21, 1895.

THE methods hitherto proposed for the preparation of ferrocyanides of barium and calcium are based either upon the decomposition of Prussian blue by the hydroxides of barium or calcium ; or upon double decomposition of barium or calcium salts on the one hand, and potassium ferrocyanide on the other.

It is very difficult to prepare Prussian blue free of potassium, and the double ferrocyanides of barium or calcium with potassium are formed more readily than the simple salts. Even when the simple salts are formed, if any potassium salt has been used in the preparation, it is almost impossible to remove the whole of the potassium by recrystallization.

After trying various other methods for the preparation of barium ferrocyanide, and having very poor success, I undertook, at the suggestion of Dr. Launcelot Andrews, to prepare it according to the following method :

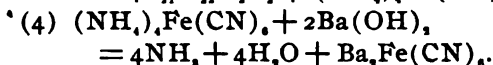
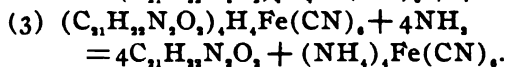
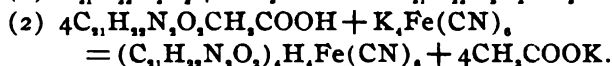
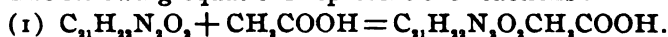
This method depends upon the formation of the normal strychnine ferrocyanide, the decomposition of this with ammonia, and the decomposition of the ammonium ferrocyanide by means of barium hydroxide. Strychnine was converted into the acetate by gently heating with water and the calculated amount of acetic acid. This salt, though one of the most soluble salts of strychnine, readily separates in the crystalline form from comparatively dilute solutions when allowed to cool, so it is best to keep it warm. A solution of the calculated amount of potassium ferrocyanide was added to the strychnine acetate, allowed to stand in a warm place, stirred frequently, and the white crystalline strychnine ferrocyanide, filtered and washed. After washing, the strychnine ferrocyanide was thoroughly mixed with ammonia water in excess, which decomposed it forming ammonium ferrocyanide and precipitating strychnine, which was easily separated from the solution of ammonium ferrocyanide, and could be used over again.

The solution of ammonium ferrocyanide, with excess of ammonia, was then boiled with a solution of the calculated

amount of barium hydroxide until no more ammonia was given off. The solution was allowed to cool, decanted from the crystals, and the mother liquid further evaporated. The crystals were dried in the air. They were found to contain a very slight amount of barium carbonate. On analysis, they gave 9.43 per cent. of iron and 46.98 per cent. of barium, which corresponds very closely to a salt of the composition represented by the formula  $\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ , and which is described in Wurtz Dict. de Chim., p. 1090.

The barium ferrocyanide can be easily prepared by this method. The main objections to this method are the bulk of liquid required to dissolve the strychnine salt, and the chance for the formation of barium carbonate during the boiling of the ammonium ferrocyanide solution with barium hydroxide. This last objection can be largely avoided by boiling in a large flask, not with the direct flame, but by passing in a current of live steam. This latter method also has the advantage of inducing the formation of better crystals of barium ferrocyanide.

The following equations represent the reactions :



Quinoline ferrocyanide was prepared in a similar manner, and this was treated directly with barium hydroxide solution, and the attempt made to get rid of the quinoline by distilling. A large amount of Prussian blue was formed, however, and the mass was thrown away. No other attempt was made using quinoline, as it was then thought that dimethylaniline would answer.

This latter method is the easiest tried and leaves little to be desired. Dimethylaniline is mixed with water, and hydrochloric acid added in slight excess. This solution then mixed with potassium ferrocyanide solution, the whole filtered and the precipitate washed with the least possible amount of water, then with alcohol, and finally with ether, and dried between pieces of filter-

paper. As little water as possible must be used, as the salt is rather soluble.

#### ANALYSIS OF THE DIMETHYLANILINE SALT.

Into a beaker was put 0.2220 gram with about one gram pure calcium carbonate, titrated with standard silver nitrate (one cc. = 5.829 milligrams sodium chloride) using potassium chromate as indicator. Required 18.4 cc. The end reaction was not very sharp, and after standing over night the red color disappeared. Then added more of the silver solution, making a total of 19.5 cc. One cc. of the above silver nitrate solution would be equivalent to 11.26 milligrams di-acid dimethylaniline ferrocyanide. Therefore the 19.5 cc. would correspond to 0.21957 gram.

Taken, 0.1325 gram mixed with water and two cc. dilute sulphuric acid added. Then added 17.18 cc. silver nitrate solution and two cc. solution of iron alum, titrated back with solution of potassium thiocyanate corresponding to the silver nitrate solution. Required six and one-tenth cc. Therefore 11.08 cc. silver nitrate solution used up by salt. In this the end reaction was not sharp.

Taken, 0.1341 gram salt. Treated as above except filtered before titrating back silver nitrate. Sixteen cc. silver nitrate added, four and one-tenth cc. potassium thiocyanate required. Therefore 11.9 cc. silver nitrate solution used, which corresponds to 0.1340 gram of the di-acid salt.

Mixed 0.1350 gram with water and titrated with tenth normal sodium hydroxide, using phenolphthalein as indicator.

Required twelve cc. which corresponds to 0.1351 gram of the di-acid salt.

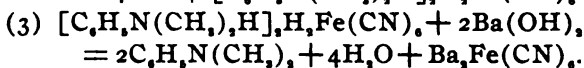
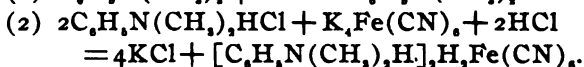
The compound is, therefore, the di-acid dimethylaniline ferrocyanide  $[C_6H_5N(CH_3)_2H]_2Fe(CN)_6$ , a white crystalline salt, which is somewhat soluble in water.

#### PREPARATION OF BARIUM FERROCYANIDE BY THE DIMETHYLANILINE FERROCYANIDE METHOD.

30.5 grams di-acid dimethylaniline ferrocyanide is mixed with barium hydroxide solution containing 22.5 grams barium hydroxide and shaken violently for some time in a flask or separatory funnel. Most of the barium ferrocyanide crystallizes out

directly and can be filtered from the liquid. The dimethylaniline is recovered by shaking the liquid with ether, which also causes more of the barium ferrocyanide to separate.

The crystals of barium ferrocyanide should be well washed, first with a little water and then with alcohol. The following equations express the reactions taking place :



Barium ferrocyanide  $[\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}]$  crystallizes in oblique rectangular prisms belonging to the monoclinic system. The crystals are unaltered in the air at ordinary temperature, lose eleven-twelfths of their water at  $40^\circ \text{C}.$ , the rest of the water is not driven off until the salt begins to decompose. The solubility varies from one in 584 parts cold water to one in 116 parts boiling water.<sup>1</sup> Dammer gives the solubility as varying from one in 1000 parts water at  $15^\circ$  to one in 100 at  $75^\circ$ .

#### SOLUBILITY OF BARIUM FERROCYANIDE.

Some solubility determinations were made on the salt prepared as above. The apparatus used was, I believe, devised by Dr. Launcelet Andrews. The apparatus consists of two Woulff bottles, *A* and *B*. *A* has three necks. The middle neck contains a perforated stopper holding a thermometer, the bulb of which goes nearly to the bottom of the bottle. The left hand neck has a stopper carrying a short glass tube which can be connected with the suction pump. The right hand neck has a stopper with a tube passing through and reaching to the bottom of the bottle; in fact, it is better to have the tube touch the bottom. This tube is connected to a tube passing through one of the necks of *B*, the other neck of *B* has a tube passing nearly to the bottom of the bottle. Water is put in the two Woulff bottles, and in *A* a larger amount of the salt to be tested than can be dissolved by the water. The whole apparatus is then put in a vessel of water, and air drawn through for several hours. The water in *B* preventing any evaporation from *A*. The current of air is then

<sup>1</sup> *Wurtz Dict. de Chim.*, p. 1091.



stopped long enough to allow the undissolved portion to settle. A measured amount of the clear liquid taken out, noting the temperature, evaporated and residue weighed.

	Amount solution.	Tempera- ture.	Residue. grams.	Parts water.
I.	5 cc.	18° C.	0.0194	257.7
II.	5 cc.	18° C.	0.0198	252.5
III.	30 cc.	18° C.	0.1190	252.1 Added 50 cc.
IV.	25 cc.	17° C.	0.0936	267.0 Water to A.
V.	25 cc.	19° C.	0.0930	268.8
VI.	25 cc.	16° C.	0.0924	270.5

These results fall within the limits as given by Wurtz.

#### PREPARATION OF CALCIUM FERROCYANIDE.

Twenty-three grams of di-acid dimethylaniline ferrocyanide mixed with water and milk of lime prepared from six grams pure lime. The mixture shaken violently in a flask, allowed to stand some time, filtered, shaken with ether to separate the dimethylaniline, separated from ethereal solution with separatory funnel, evaporated down in flask, carbon dioxide passed through, again boiled, filtered, and evaporated to about fifty cc. Alcohol then added, which causes crystals to separate. Then crystals dried between filter-paper. The crystals are of a pale yellow color and are very soluble in water. When a saturated solution is allowed to stand for a long time at the temperature of the laboratory, large flat crystals are deposited.

#### NOTE ON THE SEPARATION OF IRON AND ALUMINUM.

Since strychnine ferrocyanide is almost insoluble and is easily filtered, it may possibly be used to separate iron and aluminum in the following manner:

The solution containing ferric and aluminum salts is treated with excess of strychnine ferrocyanide. The Prussian blue thus formed can be filtered with ordinary filter-paper and the aluminum precipitated by ammonia from the filtrate. By this method I have easily gotten perfectly white aluminum oxide; but have not as yet gotten the conditions for a complete quantitative separation.

I wish in conclusion to express my thanks to Dr. Launcelot Andrews, who, by his advice and assistance, rendered this work possible.

## ON THE FORMATION OF LAYERS IN MIXTURES OF ACETIC ACID AND BENZENE.

BY C. E. LINEBARGER.

Received October 21, 1895.

DUCLAUX<sup>1</sup> states in reference to mixtures of benzene and acetic acid that "at temperatures from  $15^{\circ}$ – $20^{\circ}$  these two liquids are soluble in every proportion with each other. If a mixture of equal volumes of the two substances be cooled to about  $11^{\circ}$ , the mixture, until then homogeneous, becomes troubled all of a sudden and separates into two nearly equal layers;  $0.2^{\circ}$  of interval of temperature at most separate the two states." Duclaux then proceeds to give the results of his analyses of the two layers, as well as other results and discussions.

This account has been universally accepted, and it has passed into standard text-books that mixtures of benzene and acetic acid present at certain temperatures the phenomenon of layer-formation. This is not, however, according to fact; mixtures of *very pure* acetic acid and benzene do not separate into layers even at temperatures as low as  $20^{\circ}$ . Duclaux's observations were not made on binary mixtures of acetic acid and benzene, but upon *ternary* mixtures of *water*, acetic acid, and benzene.

A certain theoretic importance attaches itself to this question. In the course of an investigation of the vapor-tensions, both partial and total, published a few months ago in this Journal, the results found with mixtures of benzene and acetic acid were such as to preclude the possibility of layer-formation in this case. Accordingly, I have carried out some experiments on the exposure of mixtures of acetic acid, benzene, and water to varying temperatures to ascertain under what conditions of concentration and temperature, layer-formation takes place.

A cylindrical phial provided with a good cork was filled about two-thirds full of mixtures of acetic acid<sup>2</sup> and benzene.<sup>3</sup> The tube was enclosed in another larger tube, so as to prevent any possible contamination of the contents of the first tube with the baths or freezing mixtures. Several mixtures of different concentrations were exposed to a temperature of  $-20^{\circ}$ , but in no case did there occur a separation into layers.

<sup>1</sup> *Ann. chim. phys.* [5]. 7, 267, 1876.

<sup>2</sup> Purified by repeated crystallization until melting-point was not perceptibly changed no matter what the relative proportions of solid and liquid acid was.

<sup>3</sup> Purified by repeated treatment with strong sulphuric acid, repeated crystallizations and distillation over sodium.

14.6225 grams of a mixture containing 7.6037 grams of acetic acid and 7.0188 grams of benzene were placed in the tube described above and a few centigrams of water were added successively, the mixture being exposed to the temperature of a mixture of ice and salt, *i. e.*, about  $-20^{\circ}$ , after each addition of water. Not until 0.7226 gram of water had been added did there occur a separation into layers, which persisted even at  $0^{\circ}$ , but disappeared a few degrees above.

Now, Duclaux was fully aware that the presence of water rendered it possible to cause layer formation even at temperatures above  $11^{\circ}$ , for he writes: "It is indeed not necessary to have recourse to cold to obtain the separation, and the state of unstable equilibrium in which these liquids are, can be destroyed by the addition of a third substance, as, for example, water.

"A single drop of water suffices to cause a mixture of 10 cubic centimeters of benzene and of 10 cubic centimeters of acetic acid to become troubled.

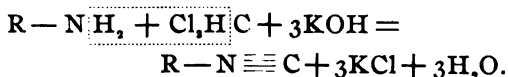
"Acetic acid crystallizing at  $14^{\circ}$  always gives a limpid solution with benzene. If it crystallizes only at  $12^{\circ}$  the mixture of equal volumes remains troubled."

Now, acetic acid melting at  $14^{\circ}$  contains not inconsiderable quantities of water, so that the behavior just described by Duclaux is what is to be expected under the circumstances. If Duclaux had taken the trouble to raise the melting-point of his acid by a few fractional crystallizations, and had employed this purified acid, there would have been one less error and its rectification encumbering the pages of chemical journals.

#### SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETINE, QUININE SULPHATE, ETC.

By F. S. HYDE.  
Received October 29, 1895.

THE test made by boiling the substance with caustic potash and chloroform is one of the most important in the scheme given below. It is known as the "carbylamine reaction" or "isonitrile test," and is common to those compounds which are classed as *primary amines* ( $R-NH_2$ ).



SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETINE, QUININE SULPHATE, ETC.

Pure substance.	Melting-point. C.	Solubility in water.	Solution of substance in water.			
			Boiled with excess caustic potash and few drops chloro- form.	Ferric chloride.	Dilute nitric acid.	Bromine water.
Acetanilide (Phenylacetamide) $C_6H_5NH.COCH_3$	113°	Soluble in cold; more so in hot.	Odor of isonitrile.	Yellow solution. Red on boiling.	Colorless.	White crystals. Para-brom- acetanilide.
Exalgine (Methyl phenylacetamide) $C_6H_5N(CH_3).COCH_3$	101°	Not very soluble, cold; easily solu- ble, hot.	No odor of iso- nitrile. Class of secondary amines.	Yellow solution. Cloudy red on boil- ing.	Colorless.	No precipitate.
Phenacetine (Acetylparaamidophenetol) $C_6H_4(OC_2H_5).NH.COCH_3$	135°	Soluble with difficulty.	Odor of isonitrile.	Yellow solution Blood-red on boil- ing.	Cloudy yellow solution. Crystals of nitro compound.	No precipitate.
Phenecol hydrochloride (Glycocolparaamidophene- tol) $C_6H_4<OC_2H_5$ $NH.COCH_3, NH_2, HCl$	No. M. P. HCl Comp.	Very soluble.	Odor of isonitrile.	Yellow solution. Darkens and orange precipitate on boiling.	Colorless.	No precipitate.
Salol (Phenol salicylate) $C_6H_4.OH.COOC_6H_5$	43°	Soluble with difficulty.	No odor of iso- nitrile. Yellow solution.	Yellow solution. Blood-red on boil- ing.	Colorless.	No precipitate cold; white cloudy compound on boil- ing.
Resorcin (Metadioxybenzene) $C_6H_4(OH)_2$	118°	Easily soluble.	No odor of iso- nitrile. Carmine-red solution.	Dark violet. Yel- lowish on adding drop of sulphuric acid.	Yellow solution.	Yellowish precipi- tate dissolving im- mediately.
Quinine sulphate $C_{20}H_{24}N_2O_8.H_2SO_4$	....	Slightly soluble. With few drops of sulphuric acid dis- solves with blue fluorescence.	Base precipitates and dissolves on heating.	Yellow solution.	Colorless with blu- ish fluorescence.	Dry substance on porcelain with weak bromine water gives green coloration on add- ing two or three drops ammonia water = Thalleo- quin test.
Antipyrine (Phenylmethyldiprazolon) $HOC_6H_3N_2(CH_3)_2C_6H_5$	113°	Soluble.	Nothing.	Blood-red. Disap- pears on adding a drop of sulphuric acid.	Colorless.	Yellowish-white precipitate.

*Phenacetine*.—Contrary to some writers, phenacetine *will* give the isonitrile test, and hence cannot be distinguished from acetanilide by this reaction.<sup>1</sup>

Exalgine does not respond to this test because it is a *secondary* amine; hence a distinction from acetanilide, phenacetine, and phenocoll.

The odor of raspberries attributed to exalgine, when heated, is somewhat misleading. It is certainly aromatic, but may resemble either strawberries or mulberries.

By boiling acetanilide with an alkaline solution of sodium hypobromite (NaBrO) or with alkaline permanganate, the same odor of isonitrile is produced, but the reaction is complicated and not perfectly understood. However, it is assumed that the benzene ring constituting the nucleus of the compound is partially broken down by the strong oxidizing action of the hypobromite or permanganate, and thus furnishes the necessary carbon substitution in the formation of isonitrile.

In making the carbylamine, isonitrile, or "isocyanide" test, as it may be called, it is preferable to have the solution strongly alkaline in every case to insure a more complete decomposition as well as quicker reaction and a more perceptible odor.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME CALIFORNIA OILS.

BY WALTER C. BLASDALE.

Received September 13, 1895.

THE investigations of which I would here record the results were undertaken some two years ago with three definite objects in view; first, the accurate determination of the limits of some of the standard constants of California olive oils; second, a practical test of the application of the Babcock method of determining adulterants in butter to a similar purpose for olive oil, and finally a determination of some of the constants of three new and hitherto undescribed oils of vegetable origin. In carrying out this work I have followed in general the methods laid down by Allen for the examination of oils, introducing such

<sup>1</sup>J. Anal. Appl. Chem., 7, 354.

modifications as more recent investigations have shown to be advisable.

The oils which have been used comprise the following samples:

1. Eleven samples of pure olive oil prepared under my own supervision from six standard varieties of olives, *viz.*, Pendulina, Uvaria, Rubra, Redding Picholine, Nevadillo blanco, and Manzanillo, according to the usual method of preparing oil for the market in California. The essential difference between the samples marked "first" and those marked "second" is that the latter include oil from the pits as well as from the pulp of the olives. A small amount of warm water was added to the pomace before pressing in the latter case. These oils, as received from the press, were washed repeatedly and filtered until clear.

2. Two samples of mustard-seed oil of California manufacture.

3. One sample of oil from the kernel of the English walnut (*Juglans regia*) grown in the southern part of the state. This oil was prepared by extraction with petroleum ether.

4. One sample of oil prepared from the fruit of our live-oak (*Quercus agrifolia*) by extraction with petroleum ether. This yields a deep brown fluorescent oil, which readily solidifies at a temperature of 10° C, and on long standing deposits waxy masses.

5. Oil prepared from the pine-nuts (probably the fruit of *Pinus monophylla*) found in our markets. This is a brown drying oil of a rather unpleasant odor and taste.

6. Oil prepared by Mr. V. K. Chesnut, from the fruit of the California nutmeg (*Tumion Californicum*).

7. Ten samples of the salad oils commonly sold in our groceries, comprising the following brands:

1. "Pure Olive Oil," J. Revalk, San Francisco.

2. "Pure California Olive Oil, Alpha Brand," Merriman Mfg. Co.

3. "California Olive Oil," Merriman Mfg. Co.

4. "Sierra Madra Olive Oil," Goldberg, Liebenbaum, and Bowen, San Francisco.

5. "Coburn's Pure Olive Oil," C. W. Coburn, San Francisco.

6. "Extra Quality Oil, Huile Vierge," A Durand et Fils, Bordeaux.

7. "Fine Salad Oil," Franco American Oil Co.

8. "Cooper's California Olive Oil."

9. "Huile D'Olive Superfin," F. Aristoy, Bordeaux.

10. "Huile Vierge," De Bossel Fil's, Marseilles.

The determinations and special tests to which these were subjected are as follows:

*Specific Gravity.*—This was in all cases determined by an accurately standardized pycnometer of about fifty cc. capacity.

*Index of Refraction.*—Determined by an Abbe refractometer of the Zeiss pattern.

*Thermal Degree.*—By this I mean the increment of temperature resulting from mixing fifteen cc. of oil with five cc. of concentrated sulphuric acid in a calorimeter with constant stirring, using an initial temperature of at least 20° C. This method of carrying out the test was rendered necessary by the small quantities of many of the samples available; as the test is of no value except when compared with known oils this forms no serious objection to the results here presented. It is perhaps unnecessary to state that the same sample of acid was used in all the tests.

*Viscosity Test.*—I believe Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap formed from a standard amount of oil in detecting adulterated olive oil. At his suggestion Mr. Babcock made the test with a number of samples of commercial oils, the results of which agreed entirely with those obtained by the application of standard tests to the same series of oils.<sup>1</sup> The method which I have used, which is essentially the one adopted by Mr. Babcock, is as follows: Fifteen grams of oil are placed in a saponification flask with about thirty cc. of water containing exactly seven and a half grams of potassium hydroxide and ten cc. of alcohol and heated on a water bath until complete saponification has been effected. The resulting soap is washed into a large evaporating dish, heated until the alcohol is expelled, diluted to exactly 500 cc. at 15° C., and the viscosity of the resulting solu-

<sup>1</sup> Methods of Detecting Adulterations in Olive Oil. Report of Olive Grower's Convention, held in San Francisco, July, 1891.

tion determined by means of a torsion viscometer, the results being calculated in terms of the number of grams of sugar which it would be necessary to add to a liter of water in order to produce a solution of equal viscosity. In the case of the two mustard-seed oils, it was found necessary to dilute the solution to one liter in order to obtain a workable solution. My more recent experiences would induce me to make some few changes in this process, the most important of which would be a change in the working temperature from  $15^{\circ}$  to  $20^{\circ}$  C.

*Saponification Number.*—By this I mean the number of milligrams of caustic potash required to saponify one gram of oil. It has been determined by the standard method, operating upon two and one-half grams of oil.

*Iodine Absorption.*—For this determination I used the standard method of Hübl, basing the standard of the hyposulphite solution on pure potassium bichromate according to the method of the Association of Official Agricultural Chemists.

*Melting Point of Fatty Acid.*—For the determination of this constant I found it most satisfactory to prepare thin but wide glass tubes on the side of which a drop of the fatty acid is allowed to solidify. This is then attached to the bulb of a thermometer, placed in a water-bath and heated until a temperature is reached at which the fat begins to run down the side of the tube. Even when the greatest care is used considerable variations will be found in the results obtained from the same sample of oil.

*Elaidin Test.*—In this I have followed the method of Poutet, the one based on the use of a freshly prepared solution of mercurous nitrate. The time required for the production of a good elaidin varies considerably, and I have indicated this factor somewhat roughly in the accompanying table.

*Milliau's Test.*—The test proposed by that author and described in this Journal, 15, 153.

An inspection of the accompanying table will show that most of the constants obtained for the pure olive-oils agree fairly well with those obtained for European oils. The iodine absorption, however, is exceptional since many of the results here reported are higher than the commonly accepted European standards.



Commercial oils.			Miscellaneous oils.			Pure olive oil.		
1	Pendulins 1st.	0.9171	1.4716	47.0	648	85.58	193.52	Reaction in 4 hours
2	Uvaia 1st. and "	0.9171	1.4714	47.0	593	84.33	193.29	
3	" "	0.9171	1.4717	"	573	85.05	190.52	
4	Rubra 1st. and "	0.9171	1.4715	"	599	85.91	190.52	
5	" "	0.9171	1.4711	45.0	565	83.93	191.88	
6	Redding picholine.	0.9161	1.4711	45.0	587	83.72	190.85	
7	Nevadillo blanco 1st.	0.9163	1.4714	45.0	585	83.33	190.74	
8	" "	0.9161	1.4710	45.0	595	84.60	192.74	
9	Manzanillo 1st. and "	0.9161	1.4710	45.0	595	84.60	191.81	
10	" "	0.9161	1.4710	45.0	595	84.60	191.81	
11	Yellow mustard seed.	0.9151	1.4731	"	3151	78.97	191.90	
12	Black "	0.9151	1.4731	"	3151	78.97	191.90	
13	Walnut oil.	0.9161	1.4710	110.0	783	85.57	174.88	
14	Pine-nut oil.	0.9161	1.4710	110.0	783	85.57	174.88	
15	California nutmeg oil.	0.9161	1.4710	110.0	783	85.57	174.88	
16	" "	0.9161	1.4710	110.0	783	85.57	174.88	
17	California nutmeg oil.	0.9161	1.4710	110.0	783	85.57	174.88	
18	Revala olive oil.	0.9171	1.4716	77.0	238	94.71	193.39	
19	Merriman alpha oil.	0.9171	1.4716	77.0	238	94.71	193.39	
20	Merriman alpha oil.	0.9171	1.4716	77.0	238	94.71	193.39	
21	Sierra Madre oil. G. L. & B.	0.9171	1.4716	77.0	238	94.71	193.39	
22	Coburn's olive oil.	0.9171	1.4716	77.0	238	94.71	193.39	
23	Durand & Co.'s oil.	0.9171	1.4716	77.0	238	94.71	193.39	
24	Francisco A. Oil Co.	0.9171	1.4716	77.0	238	94.71	193.39	
25	Cooper's California oil.	0.9171	1.4716	77.0	238	94.71	193.39	
26	F. Artioy's oil.	0.9171	1.4716	77.0	238	94.71	193.39	
27	De Bosis's Bone oil.	0.9158	1.4793	45.0	583	84.09	192.12	
Specific gravity.								
Index of refraction.								
Thermal degree.								
Viscosity.								
Melting point of fat acid.								
Iodine absorption.								
Saponification number.								
Elaidin test.								
Milliau's test.								
No reaction								
Reaction in 6 hours								
Reaction in 3 hours								
Reaction in 1 hour								
Reaction in 30 minutes								
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A possible explanation may be found in the fact that many of the varieties here represented are not those commonly used for the production of oil. Similar results have been obtained by Mr. G. E. Colby.<sup>1</sup> In the application of the elaidin test striking differences were observed both in the character of the elaidin and in the length of time necessary for its production. On the one extreme are oils of the Manzanillo type which produce a perfectly solid mass within an hour, whereas the two Uvaria oils produced only a partial solidification even after six hours. The facts seem to indicate that the test is not as reliable as has been supposed.

From a comparison of the results obtained from the oils of known purity with those obtained from the commercial oils it will at once be seen that Nos. 18, 23 and 24 are heavily adulterated with cottonseed-oil. No. 20 shows strong evidences of adulteration though the percentage is not as high as in the other cases.

I think it is also shown that the application of the viscosity test to the detection of adulterated olive oils is entirely successful; the variations in the figures obtained from the different samples of pure oil are considerable but not so great as to admit of confusion with any of the adulterated oils. In addition to the figures presented in the table, I have obtained the following results: For cottonseed-oil 280, for sweet-almond oil 645, for rape-seed oil 670, for poppy-seed oil 95, for sesame oil 415, for lard oil 250, and for peanut oil 220, an array of figures which plainly shows the utility of this test. It will be seen that the only oils whose viscosity-constant approaches that of pure olive oil are almond, rape-seed and sesame. Of these the first is not likely to be used as an adulterant and the two latter are readily detected by other tests. The only oils showing a materially higher viscosity constant are the two mustard-seed oils, and it must be admitted that carefully proportioned mixtures of mustard and cottonseed-oils could not be detected by this test. The method promises to be of particular value in detecting lard oil for which we have had no satisfactory specific test.

Of the three hitherto undescribed oils No. 16 seem to agree in

<sup>1</sup> Report of California Agricultural Experimental Station, 1890.

most of its properties with other oils prepared from related plants, viz: *Pinus sylvestris*, *Pinus picea*, and *Pinus abies* in so far as these are known, and could probably be used for similar purposes.

No. 17 though obtained from a closely allied plant is an oil of quite a different character, but the data at present available is too insufficient to admit of a satisfactory prediction of its constituents. It might be of interest to note here that J. J. Rein, in a work entitled "The Industries of Japan," mentions the fact that an oil is prepared by the Japanese from the fruit of *Tunion nucifera* and used by them in their kitchens.

In conclusion I wish to express my thanks to Prof. Rising for suggestions received during the course of the work and also to the officials of the Experiment Station at Berkeley, through whose kindness I was enabled to obtain the samples of pure olive oil.

#### THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD, AND BY VOLUMETRIC METHOD.<sup>1</sup>

BY B. W. KILGORE.

Received September 30, 1895.

IN a summary statement of the results obtained last year by the members of the Association of Official Agricultural Chemists and other chemists cooperating with them by the official molybdate method on a solution of C. P. disodium hydrogen phosphate, I called attention<sup>2</sup> to the fact that the results of nearly all of the analysts (twenty-eight) were high and some of them very materially so. The larger number of these analysts were experienced in this class of work. From this and other reasons I argued that the molybdate method, as usually worked, has a tendency to give high results, and that these high results are due to an excess of magnesium in the magnesium ammonium phosphate precipitate.

For the investigation of phosphoric acid methods for this association for 1895, two chemically pure phosphate solutions and one mixed fertilizer were employed.

<sup>1</sup> For description of this method, see methods of the Association of Official Agricultural Chemists for 1895.

<sup>2</sup> This Journal, 16, 793.

No. 1 was a solution of the same phosphate worked upon last year, and contained ten grams chemically pure disodium hydrogen phosphate to the liter, the theoretical percentage of phosphorus pentoxide in this salt being 19.826.

No. 2 was No. 1 diluted with five parts of water, and therefore contained the equivalent of 3.304 per cent. phosphorus pentoxide in 50 cc.

Fifteen chemists reported forty determinations on solution No. 1, the highest of which was 20.50 per cent., and the lowest 19.75 per cent., the former being 0.674 per cent. above the theory, and the latter 0.076 per cent. below. The average of all results was 20.044 per cent., or 0.218 per cent. above the theoretical content; the variation between the highest and lowest results was 0.75 per cent.; the variation below the theory was 0.076 per cent., and above the theory 0.674 per cent. Fourteen per cent. of the determinations were within 0.05 per cent. of the theory; thirty-three per cent. within one-tenth; and fifty-six per cent. within two-tenths. On the whole these results make a slightly better showing toward accuracy than did those of last year on the same phosphate, but like the results of last year, most of them are high. In 1894 there were two results below the theory, 19.74 and 19.78 per cent.; this year there are also two, 19.75 and 19.77, the lowest of the former being 0.08, and of the latter 0.07 per cent. below the theory; while the highest results of the two years were 0.84 and 0.76 per cent. above the theory.

On sample No. 2, containing 3.304 per cent. phosphorus pentoxide, there were forty-two determinations reported, the highest of which was 3.65 per cent., or 0.346 per cent. above the theory; and the lowest was 3.20 per cent., or 0.104 per cent. below the theory. The average of all results was 3.43 per cent., or 0.126 per cent. high. Out of forty-two results on this sample, four were below the theory. These variations being 0.10, 0.02, 0.02, and 0.01 per cent.

The foregoing adds strength to the remarks made on this subject last year, that the molybdate-magnesia method gives high results in the hands of nearly all workers, and may give extremely high ones in the hands of some.

We do not believe, however, that there is any well established

method of sufficient rapidity that suits our needs better or with which we can get better results, when proper precautions are taken, than the molybdate method.

It may be of interest here to give also a brief summary of the results on these same phosphate solutions by the volumetric method as investigated this year. The results were obtained by some of the same chemists who analyzed these samples by the gravimetric method. This was the first time the volumetric method in its present form had been used by most of them.

Thirteen chemists reported thirty-one determinations on solution No. 1 and thirty-three on No. 2 by the volumetric method. Seventy-three per cent. of all the results on No. 1 were within 0.05 per cent. of the theory, and ninety-three per cent. were within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of the results were within 0.05 per cent. of the theory, and all were within one-tenth.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid," made by the writer to that association at its recent meeting.

NORTH CAROLINA EXPERIMENT STATION,  
Raleigh, N. C.

## THE VOLUMETRIC ESTIMATION OF MANGANESE.

BY GEORGE AUCHY.

Received October 22, 1895.

IN this Journal, 17, 5, Mr. W. H. Thomas describes his experience with Low's and with Volhard's method of determining manganese. The latter he finds reasonably accurate. The former not at all so. Some ten or twelve years ago, in the transactions of the American Institute of Mining Engineers, Williams' method in steel, which is based on the same principle as Low's method in ores, was the subject of considerable controversy; some claiming, others disputing its accuracy. And although the weight of the testimony seemed to be in favor of the method, nevertheless, the close of the discussion left the matter still somewhat in doubt.

Are methods based upon this principle reliable? Mr. Thomas'

experience with Low's method is further evidence to the contrary. But as regards Williams' method, perhaps it may be said that Mr. Thomas' results are not in evidence, inasmuch as potassium chlorate and strong nitric acid are stronger oxidizing agents than bromine water, and may therefore be depended upon to oxidize the manganese completely to manganese dioxide, even if the latter cannot be. But Mr. Stone's and others work is against this assumption; also the following results obtained from manganese ores :

	Williams' method (practically) per cent.	Volhard's method. per cent.
Ore No. 1.....	51.71	53.04
" " 2.....	51.58	53.00
" " 3.....	44.88	46.80
" " 4.....	43.00	46.24
" " 5.....	41.22	42.64
" " 6.....	34.39	40.00
" " 7.....	44.88	46.40
" " 8.....	31.61	43.76

Among steel works chemists, Williams' method is very popular on account of its great ease and simplicity. Comparatively few, perhaps, use Volhard's method. And it is therefore important that the reliability of the former method be more fully and definitely established. So far, the evidence in its favor is strong and positive. But there is still room for doubt. More work seems to be required to fully settle the question, and it would be well for chemists who use this method, to patiently check with Volhard's method for a considerable time, (using different lots of chlorate) and communicate their results and opinions to the Society. I say Volhard's method, because the gravimetric is too cumbersome for such an extended use, and is probably more-over not any more accurate—perhaps not so much so—as Volhard's.

My own experience with Williams' method leads me to believe that it usually, but not always, gives accurate results. And I am disposed to think that if chemists who have repeatedly obtained good results with that method, and who have therefore every confidence in it, would nevertheless keep on for an extended period checking their results by Volhard's method

they would sooner or later be treated to a disagreeable surprise such as illustrated by the last four of the following results :

	Williams' method. per cent.	Volhard's method. per cent.
Heat ..... 114	0.42	0.42
Rolled steel.....	0.43	0.45
Heat ..... 116	0.50	0.50
" ..... 120	0.40	0.41
" ..... 121	0.42	0.42
Tire steel.....	0.92	0.94
Heat ..... 125	0.48	0.54
Tire ..... 125	1.04	1.20
Heat ..... 162	0.37 and 0.42	0.45
" ..... 163	0.40	0.48

With heat 163 Williams' method was given up.

With regard to the method of oxidizing to permanganate by lead oxid and titrating with arsenious solution, without having given the method actual trial, I am nevertheless convinced that it gives uniformly low results, from the fact that while it was in use at these works, 135 and 140 pounds of ferromanganese per charge was needed to bring the manganese content to the required point, working by this method, while now, with Volhard's method in use, only ninety and 100 pounds are used to bring the same result. But the lead oxid used in the method was the tetroxide. Probably by the use of dioxide, good results may be obtained.

For the benefit of chemists, who have never used Volhard's method, and who feel disposed to give it a trial, for the purpose I have suggested, I beg to call attention to certain precautions which are essential to a successful practice of the method.

1. In boiling off the nitric acid with sulphuric acid, it is very essential to avoid too much sulphuric acid, as otherwise the bumping and spattering will be so violent as to altogether spoil the test.

2. The dry mass should be taken up with *hot* water, allowing the dish first only a minute or two for cooling. If the dish be allowed to cool completely, and cold water be added, and then boiled up, very frequently a red ferric sulphate carrying much manganese will remain insoluble, no matter how much additional sulphuric acid be added. Even this precaution is value-

less, however, if the dry mass be heated too long. But this residue can be brought into solution by decanting the clear solution and then heating for some time with sulphuric acid. But to save time its separation should of course be prevented in the first place.

3. In steels high in manganese it is advisable, and in steels low in manganese it is absolutely essential that not too much zinc oxide be used; as it will separate out when the solution is heated, if much has been used, and will retard the settling of the manganese dioxide if the steel be high in manganese, and will completely prevent it if the steel be low in manganese, (0.18—0.24 per cent.) and thus make the observation of the end of the titration impossible. Before the zinc oxide is added, therefore, the solution should be in as small a bulk as convenient and be as nearly neutralized with sodium carbonate as possible.

4. When titrating with permanganate, the reddish color caused by the permanganate should be completely changed into clear yellow by shaking the flask before more permanganate is added, and at the end the liquid must be distinctly and permanently rose colored—that is, it must retain its color through a dozen good shakings. It is well, toward the end, to add the permanganate four drops at a time (when two drops equal one-tenth cc.) till the distinct rose-tint is reached, and then deduct one-tenth cc. from the reading of the scale.

It may be a convenience to state the method in detail. Take exactly three and three-tenths grams in a six-inch evaporating dish. Cover and dissolve on the hot plate in forty cc. of nitric acid containing a little more than half of strong acid. Add eight cc. (no more) strong sulphuric acid. If, however, the liquid becomes cloudy on boiling, the violent bumping and spattering before referred to will inevitably occur as the boiling progresses further. Add then at once some strong hydrochloric acid, and transfer to a wire gauze, where boil down rapidly over a good strong flame till the mass is nearly dry—a little pastiness still remaining here and there. It is best to remove the cover when the liquid gets pasty. Allow to cool a minute or two. Take up with hot water and boil a few minutes. Cool by placing in a larger dish of cold water. Pour into a 500 cc. measuring flask. Nearly neu-



tralize with sodium carbonate. Add zinc oxide emulsion until sudden stiffening of the solution. Dilute to the mark. Pour in a dry beaker, mix with rod, and pour through a very large ribbed filter into a 250 cc. measuring flask. When the liquid has reached the mark, withdraw, and transfer to a 500 cc. Erlenmeyer flask. Heat to boiling. Add nearly the full amount of permanganate of strength exactly 0.0055, if the percentage of manganese is approximately known. If not add only one and a half cc. permanganate, and boil until the manganese dioxide separates in flakes, and the liquid becomes yellow. Finish the titration shaking after each addition of permanganate till the yellow reappears. The number of cc. permanganate divided by ten will give the percentage of manganese.

Where the method is in daily use, it will be well to use for neutralizing before adding zinc oxide common sal soda instead of the expensive chemically pure carbonate. But this will add about 0.03 per cent. to the manganese, and must be determined and deducted. The sal soda can be procured at grocery or drug stores. Two pounds in two liters of water (and filtered) is a convenient solution.

The impurity is best determined by doing a steel with pure sodium carbonate, then with the sal soda. For convenience, the amount of the soda solution required to nearly neutralize the manganese solution is noted, and that amount is then at once added in subsequent determinations.

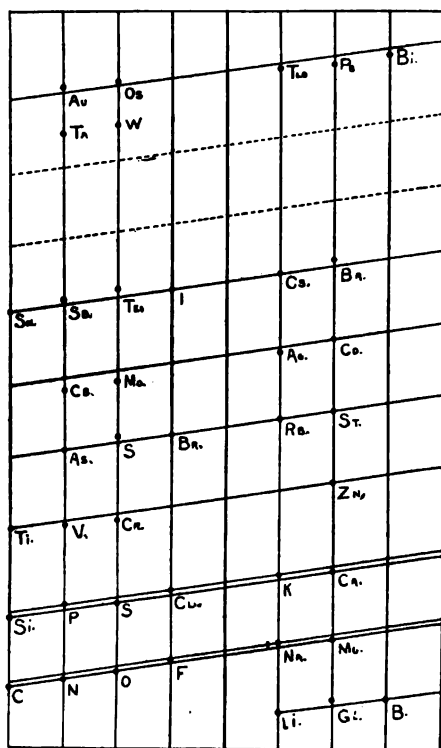
## AN EARLY AMERICAN ARRANGEMENT OF THE ELEMENTS.

BY F. P. VENABLE.  
Received September 23, 1895.

IN going over the papers published during the period immediately following the announcement of the Periodic Law, there is one which possesses especial interest for an American.

It is the "Synoptical Tables of the Elements" by Dr. L. R. Gibbes, of Charleston, appearing in the publications of the Elliott Society in 1875. This table had been prepared some two or three years previously for the use of his classes. In it a professor in a remote and small American college worked out for himself, evidently in ignorance of the arrangements of Mende-

leeff and Meyer, some of the most important principles of the Periodic Law. The evidence of this ignorance is presumptive; first, because his table was very crude and certainly would not have been offered to his classes had the author known of the much superior ones which had already appeared; secondly, he carefully mentions all authorities known to him and upon whom



he had drawn in the construction of his table. His library was an antebellum one and the authorities were old. Still he forestalls two or three late authors in his methods of graphic representation of the law.

His table was designed to exhibit:

1. The groups of elements.
2. The atomic weight of each element.
3. The character of each, as perissad or artiad.
4. Their atomic equivalence or atomicity.
5. The electro-chemical character.

In his table the elements were arranged in the order of their atomic weights, but with a good many gaps unfilled, from imperfect knowledge. He remarks upon the "continuity or regularity in the series of numbers" as being very striking.

In his diagram he gives upon the horizontal axes, right and left, from the centre, the positive and negative electricities as abscissas. The atomic weights are laid off as ordinates upon the vertical axes, rising from a zero atomicity. This gives the ele-

ments in an ascending scale of atomic weights, though they are broken up into three series. With much acute reasoning and insight, Gibbs shows that the three series may be exhibited in continuity as one, that is, by the use of an Archimedean Spiral whose radius vector increases by sixteen units in one revolution.

This is the arrangement of Lothar Meyer and de Chancourtois and the spiral suggested by Mendeleeff. His diagram will, on investigation, be seen to be based on the same principles as those of Spring, Reynolds and Crookes.

The author goes further and anticipates some of the geometrical work of Haughton. He observes that no linear equation can be constructed to give more than rude approximations to the atomic weights, and that to construct curves, two points of inflection or contrary curvature must be given. These are the serpentine cubics afterwards worked out by Haughton.

He cautions against laying too much stress upon such arithmetical and geometric exercises.

It seems remarkable that, with so imperfect a table, so much of the later work, done with the perfected tables given by the authors of the Periodic Law, should have been anticipated, especially when we notice how slight was Gibbs' idea of periodicity. He gives in his table seven groups, it is true, four negative and three positive, but they are very poorly filled out, and he shows no completed period of seven in the entire table. His observed regularities can scarcely refer to periodicity, still he makes some mention of what Meyer calls double periodicity, though of course not under this name.

Dr. Gibbs was a professor in the College of Charleston, a fine physicist and a thoughtful chemist. These "Synoptical Tables" which he built up upon the work of Dumas, Gladstone, Cooke, Odling and Barker, speak highly for his insight and power of reasoning.

UNIVERSITY OF NORTH CAROLINA, Sept. 1895.

10-27-95

**ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.<sup>1</sup>**

BY B. W. KILGORE.

Received September 30, 1895.

IN November, 1894, the writer published<sup>2</sup> some results of an investigation of the method on this principle as originally described<sup>3</sup> by Mr. H. Pemberton, Jr., and as modified by the writer, together with an account of some work upon molybdic solutions and temperatures of precipitation best suited for obtaining ammonium phosphomolybdate uncontaminated with molybdic acid.

These investigations were undertaken in part by the writer as reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1893-94, to see if the volumetric method was sufficiently accurate and trustworthy, or if it could be developed into a sufficiently reliable method to be used by these chemists in their official work.

The present official gravimetric method is rather long and often gives quite varying results in the hands of different analysts and not always the most concordant ones in the hands of the same analyst. These two objections to the molybdate method, together with the immense volume of phosphoric acid work which has to be done in connection with "Fertilizer Control Stations" and fertilizer factories makes it doubly important that a quick and accurate method for phosphoric acid estimation should, if possible, be found.

The volumetric method seemed to promise well, and it was accordingly sent out, both as originally described by Pemberton and as modified by the writer, to various official and other chemists interested in phosphoric acid work for trial. Three phosphate samples were prepared upon which to conduct the investigations.

No. 1 was a mixture of cottonseed meal and castor pomace, containing about two and a half per cent. phosphorus pentoxide.

No. 2 was an acid phosphate containing about seventeen per cent. phosphorus pentoxide.

<sup>1</sup> This with some additional matter will appear in a bulletin from the North Carolina Experiment Station.

<sup>2</sup> This Journal, 16, 765.

<sup>3</sup> This Journal, 15, 382.

No. 3 was a solution of chemically pure disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), containing 19.826 per cent. phosphorus pentoxide.

The results obtained in this laboratory<sup>1</sup> on these samples by the different methods and presented to the association are shown in Table I.

These results, with a few exceptions, indicate well for the volumetric method, especially the method as described by the writer, there being only one result (20.10 per cent. on sample 3) by this method without the reasonable error of analysis. The larger percentage of the results however on samples 2 and 3 by the method as carried out by Pemberton are high.

The corresponding results on these samples by some sixteen other chemists were not as a whole nearly so encouraging as those presented above, which was likely due to the greater familiarity with the volumetric method in this laboratory.

Then, too, the very large amount of wash water (amounting in some cases to more than a liter) found necessary by a great many to remove free acid from the precipitate made the washing tedious and gave the method little or no advantage in most hands as regards time over the gravimetric method and no advantage in point of accuracy, the latter being especially true when it is made known that now and then unaccountably high results would be obtained by many in the midst of good ones. Notwithstanding these difficulties, most of the chemists who had tried the volumetric method in the different forms in which it was worked up to this time, considered their results on a whole as encouraging, but not such as to give them any considerable faith in the method, especially for high percentages.

At this point the writer again commenced studying further the volumetric method in its various phases and trying numerous modifications to it.

The results obtained last year<sup>2</sup> by the writer's modification of the Pemberton method, consisting of a different molybdic solution and temperature of precipitation, were much more uniform and satisfactory than those obtained by the original Pemberton method on the same samples.

<sup>1</sup> The results of other chemists on these samples will be found in Bul. 43, Div. Chem. U. S. Dept. Agr., page 81.

<sup>2</sup> This Journal, 16, 767.

TABLE I. TOTAL PHOSPHORIC ACID IN ABOVE SAMPLES 1, 2, AND 3.

Analyst.	No. 3.						No. 2.						No. 1.					
	Methods and washings.						Methods and washings.						Methods and washings.					
	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.
W. M. Allen ...	Per cent. ....	Per cent. ....	cc. ....	Per cent. ....	cc. ....	Per cent. ....	Per cent. ....	cc. ....	Per cent. ....	cc. ....	Per cent. ....	Per cent. ....	cc. ....	Per cent. ....	cc. ....	Per cent. ....	Per cent. ....	cc. ....
	19.93 <sup>2</sup>	20.00	650	17.13	...	17.13	...	...	17.15	...	...	...	650	17.15	...	2.52	...	350
	19.94 <sup>3</sup>	20.15	850	17.18	...	17.18	...	...	17.00	...	2.52	...	to 800	17.00	...	2.55	...	350
	19.93	...	...	17.15	...	17.15	...	...	17.10	...	...	...	...	17.10	...	2.55	...	400
F. B. Carpenter	19.91	...	...	17.10	...	17.10	...	...	17.15	...	2.61	...	...	17.15	...	2.58	...	...
	20.06	20.35	650	17.17	17.20	17.17	17.20	500	17.15	450	2.42	...	...	17.15	450	2.50	250	...
	19.93	20.15	850	17.12	17.40	17.12	17.40	500	17.10	450	...	...	...	17.10	450	2.45	250	...
	19.81 <sup>4</sup>	20.15	850	16.98 <sup>1</sup>	...	16.98 <sup>1</sup>	...	...	16.97	450	...	...	...	16.97	450	...	...	...
	19.83 <sup>4</sup>	20.10	1,000	16.98 <sup>1</sup>	...	16.98 <sup>1</sup>	...	...	17.00	500	...	...	...	17.00	500	...	...	...
	19.91 <sup>3</sup>	...	...	...	...	...	...	...	17.10	500	...	...	...	17.10	500	...	...	...
	19.85 <sup>3</sup>	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
C. B. Williams.	20.03 <sup>3</sup>	...	...	...	...	...	...	...	17.10	500	...	...	...	17.10	500	...	2.50	500
	20.05 <sup>3</sup>	...	...	...	...	16.96 <sup>1</sup>	...	...	17.10	500	...	...	...	17.10	500	...	2.50	...

<sup>1</sup> The "white" precipitate was dissolved and reprecipitated.<sup>2</sup> Precipitated with magnesia mixture/direct.<sup>4</sup> One gram citric acid added before precipitating with magnesia mixture.

This modified method gave quite as good results in the writer's hands as did the official method. It was therefore decided to use this modified procedure, that is, precipitation at 60° C., and with the official molybdic solution as the starting-point for the investigation.

Knowing that the deposition of molybdic acid was the cause of the trouble in the volumetric method, various ways of getting rid of it were tried. One attempt was to dissolve the ammonium phosphomolybdate in the least possible quantity of concentrated ammonia, thus changing any molybdic acid to ammonium molybdate, acidifying with nitric acid, evaporating to dryness and heating to drive off all nitric acid. This was not practicable for other reasons than that molybdic acid was again formed from the ammonium molybdate on heating to a temperature that would drive off nitric acid. Distillation of the ammonia from the "yellow precipitate" and the calculation of the phosphoric acid from that would not do in that the deposit of molybdic acid carries ammonium molybdate with it. Finally it was determined to try to find wash solutions, which would dissolve molybdic acid, but not ammonium phosphomolybdate.

Using a chemically pure disodium hydrogen phosphate containing 19.826 per cent. phosphorus pentoxide, the following results were obtained with different strengths of nitric acid for washing, finishing with potassium nitrate solution and water to remove nitric acid.

## WASH SOLUTIONS.

No. of times washed with water by decantation.	No. of times washed with dilute nitric acid by decantation.	No. of times washed with three per cent. potassium nitrate by decantation.	Washed on filter with water. cc.	5 cc. 1.42 sp.-gr. nitric acid in 100 cc. water.	10 cc. 1.42 sp.-gr. nitric acid in 100 cc. water.	20 cc. 1.42 sp.-gr. nitric acid in 100 cc. water.	Washed with water only.
				per cent.	per cent.	per cent.	
.	1	2	275	....	....	19.80	....
1	1	1	275	....	19.84	....	....
2	1	.	275	19.98	....	....	....
.	2	1	400	....	....	19.80	....
.	2	1	400	....	19.87	....	....
1	2	.	275	19.80	....	....	....
3	.	.	400	....	....	....	19.98
.	2	1	230	....	19.87	....	....
.	2	1	350	....	19.83	....	....
3	.	.	700	....	....	....	19.93
3	.	.	550	....	....	....	19.87

The washing with dilute nitric acid and three per cent. potassium nitrate solution was always by decantation, using fifty cc. to seventy-five cc., agitating thoroughly and allowing the precipitate to settle completely each time. When the washing was with water alone, the results are high, while washing twice by decantation with the wash containing ten cc. 1.42 sp. gr. nitric acid in 100 cc., once by decantation with three per cent. potassium nitrate solution, and then with about 300 cc. water on the filter, the results are close to theoretical ones.

*Solubility of Molybdic Acid in Various Wash Solutions.*—It now seems important to investigate the solubility of molybdic acid in various solutions which might be used for washing. The results of this work are contained in the table below and the solubility is expressed in terms of the number of cc. of the standard volumetric alkali neutralized by the molybdic acid dissolved. 100 cc. of this alkali equals 32.38 cc. normal alkali.

SOLUBILITY OF  $\text{MoO}_3$  IN VARIOUS WASH SOLUTIONS.

1	No. $\text{MoO}_3$ used.	Amount of $\text{MoO}_3$ , grams.	Amount of solution cc.	Time of standing, hours.	Water.	2 cc. 1.42 sp. gr. nitric acid in 100 cc. Water.	5 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	10 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	20 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	2.5 per cent. potassium nitrate.	5 per cent. potassium nitrate.	5 per cent. sodium nitrate.
1	2	100	1	1.4 <sup>1</sup>	..	..	..	5.6	6.8	0.4 <sup>2</sup>	0.5 <sup>2</sup>	0.5 <sup>2</sup>
2	1	100	2	..	7.4	8.1	8.8	..	..	..	7.5 <sub>1</sub>	..
3	1	100	1	..	..	..	2.8 <sup>3</sup>	..	3% $\text{KNO}_3$	..	..	..
4	1	100	1	0.45 <sup>3</sup>	0.8	1.5	2.0, 2.3	2.8	0.92	..	..	..
5	1	100	1	..	2.4 <sup>3</sup>	3.55 <sup>3</sup>	5.15	6.3	0.92 <sup>3</sup>	..	..	..
6	1	100	1	..	2.9 <sup>3</sup>	4.7 <sup>3</sup>	7.3	8.85	1.0 <sup>3</sup>	..	..	..
7	1	100	1	..	..	..	2.2	..	0.8	..	..	..
8	1	100	1	..	..	..	2.2	..	0.7	..	..	..
9	1	100	1	..	..	..	2.8	..	0.8	..	..	..
10	1	100	1	..	..	..	2.8	..	0.8	..	..	..

<sup>1</sup> Stood eighteen hours and then filtered turbid, though double filter was used; result too high.

<sup>2</sup> Filtered turbid; results too high.

<sup>3</sup> Used as in washing the yellow precipitate. One portion of 100 cc. was added, stirred and allowed to stand fifteen minutes, and filtered off; then another 100 cc. portion was added and titrated in the same way.

<sup>4</sup> Stood twenty-four hours before a clear filtrate could be obtained.



These solubility determinations were made by allowing 100 cc. of the respective solutions to stand in a beaker with the molybdic acid for the time indicated in the table, stirring once or twice to keep the molybdic acid in contact with the liquid, but allowing sufficient time before filtration for most of it to settle to the bottom of the beaker. The washes were then filtered through double filters, evaporated to dryness (when nitric acid was present), heated in an air-bath until nitric acid was driven off, and titrated. It was found very difficult to prevent the molybdic acid from passing through the filter when water was used as the solvent. It would remain suspended in a very finely divided state in water for twenty-four hours and pass through the filter. The results for the water solubility are therefore generally too high. This is also true to a less extent of the solubility in two and a half, three, and five per cent. potassium nitrate solutions, and in the five per cent. sodium nitrate solution; and to a still less extent of the solubility in two and five cc. nitric acid solutions.

The results are not all uniform but fairly so when the same molybdic acid was used. None of these molybdic acids were pure.

Numbers 1 and 2 contained considerable quantities of ammonium nitrate and ammonium molybdate, and perhaps some sodium molybdate. Numbers 3, 4, and 5 were washed by decantation for a day or more with large quantities of dilute nitric acid, and finally once or twice with water, and contained, so far as we ascertained, only ammonium molybdate as impurity. The impurities did not, we think, materially affect the solubility of these acids in the wash solutions. The results, at any rate, are of value in showing the comparative solvent action of the different washes for molybdic acid under conditions similar to those in which they are used in the method.

They show that water, and sodium and potassium nitrate solutions have very little solvent action upon molybdic acid; while that of the stronger nitric acid solutions is quite considerable. After all, these results may represent more nearly what we want than they would, had pure molybdic acid been

used ; for in the volumetric method it is not a solvent for molybdic acid alone that is wanted, but for a mixture of molybdic acid and ammonium molybdate perhaps in quite variable quantities.

Of the dilute nitric acid washes, the one containing ten cc., 1.42 sp. gr., nitric acid in 100 cc. of the wash was adopted because it possesses good solvent power for molybdic acid and is of practically the same acidity as the solution in which the precipitation of ammonium phosphomolybdate is made in the official method. The official molybdic solution contains nearly fifteen cc., 1.42 sp. gr., nitric acid in fifty cc. ; and a solution requiring fifty cc. of molybdic solution to precipitate the phosphoric acid in it usually has a volume near 100 cc. ; the two would give a volume of 150 cc, containing about ten cc. nitric acid in the 100 cc.

We know that precipitation is complete in a solution of this acidity, and no solvent action takes place on long standing. It therefore seems reasonable to conclude that nitric acid of the same strength would exert little or no solvent action on the ammonium phosphomolybdate in the short time required to wash the precipitate.

#### SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN THE FOREGOING WASH SOLUTIONS.

It now appeared desirable to investigate the solubility of ammonium phosphomolybdate in these same wash solutions. This was done by preparing a pure phosphomolybdate from sodium phosphate by precipitating with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation with dilute nitric acid, and finally with water to remove most of the nitric acid, and drying to constant weight at 130° to 150° C. This phosphomolybdate contained 3.789 per cent. phosphorus pentoxide, the theory being 3.783, showing that it was practically pure. The solubility is expressed in terms of the number of cc. of standard volumetric alkali required to neutralize the phosphomolybdate dissolved. One cc. of this alkali equals one milligram phosphorus pentoxide.

## SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN WASH SOLUTIONS.

	Amount of solution.	Time of standing—hours.	Water at 65° C.	Water at laboratory temperature, about 27° C.	2 cc. HNO <sub>3</sub> in 100 cc. wash.	5 cc. HNO <sub>3</sub> in 100 cc. wash.	10 cc. HNO <sub>3</sub> in 100 cc. wash at 65° C.	10 cc. HNO <sub>3</sub> in 100 cc. wash at laboratory temperature.	20 cc. HNO <sub>3</sub> in 100 cc. wash.	3 per cent. KNO <sub>3</sub> solution.
0.75 to 1.4 grams substance stood in 500 cc. of the solution for the time indicated, and 200 cc. was taken each time for the test.	200	24	5.2 <sup>1</sup>	0.85 <sup>1</sup>	0.2	0.25	20.1	0.6	0.75	0.5
	200	106	6.0 <sup>2</sup>	3.0 <sup>2</sup>	2.05	5.5	16.75 <sup>2</sup>	6.75	11.45	4.35
Results from allowing precipitates from 20 per cent. phosphate to stand in these solutions.	200	1	..	none	..	none	..	none	none	none
	200	1	..	trace	..	trace	..	trace	trace	trace

From 0.75 to one and four-tenths grams of the prepared phosphomolybdate was shaken up in flasks with 500 cc. of the wash solutions. Two hundred cc. of this was filtered off at the end of twenty-four hours and 106 hours respectively, evaporated to dryness (when nitric acid was present), the nitric acid driven off, and the residue titrated. The phosphomolybdate settled in only two or three of these washes in less time than twenty-four hours, and even then the very fine particles remained suspended in the water solutions, and it was found impossible to get clear filtrates from them. The results for water-solubility are therefore too high. For the reason just stated the solubility of ammonium phosphomolybdate in the washes could not be determined for the times they would ordinarily stand in contact with the precipitate in washing by the use of the pure molybdate. If, however, the solubility of even this pure phosphomolybdate was proportional to the time of standing in the washes, the amount that would have been dissolved by all the washes (dilute nitric acid, potassium nitrate, and water) used in washing a precipitate in the ordinary thirty minutes required for washing could hardly have been found. I calculated that on this basis a plus correction of

<sup>1</sup> These filtered very turbid; they had not settled in twenty-four hours.

<sup>2</sup> These stood at laboratory temperature (about 27° C.) after first twenty-four hours.

<sup>3</sup> Filtered turbid; results too high.

about 0.016 per cent. would be necessary on basis of two-tenths gram substance.

The solubility of the "yellow precipitate" just as it is precipitated in ordinary work along with the salts carried down with it was also determined in the wash solution by allowing 200 cc. of them to stand in contact with the precipitate for one-half and one hour, respectively, after stirring thoroughly. The precipitates settled completely and quickly in this way. In none of these washes could more than a trace of phosphoric acid be found. Again all the washings (3600 cc.) from six determinations of phosphoric acid in two phosphate solutions (a 3.30 per cent. and a 19.83 per cent.) were combined, evaporated down and the phosphoric acid in them determined by the gravimetric method, when 0.38 milligrams phosphorus pentoxide was found, corresponding to a plus correction of 0.03 per cent. on basis of two-tenths gram substance. A similar result was obtained from the washings from eight determinations on the same samples.

These results indicate that while the wash solutions used in the volumetric method have marked solvent power for molybdic acid, they have practically no solvent action on ammonium phosphomolybdate, and that a correction for ordinary work at least is not necessary. There is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove nitric acid. In this after washing, when all the salts have been removed from the precipitate and as much as 600 or 700 cc. has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. of water in our present manipulation of the method. We consider that 500 or 600 cc. of water may be used without this loss, but the filtrate should be closely observed when the washing goes beyond this amount.

#### INVESTIGATION OF MOLYBDIC SOLUTIONS.

Besides the comparison of the aqueous molybdate of Pember-ton with the official molybdic solution recorded in my last year's work,<sup>1</sup> nine other molybdic solutions of different formulas, in-

<sup>1</sup>This Journal, 16, 769.

cluding five or six of those most highly recommended by different analysts, and the remainder of our own making, have been tried. The formulas of these solutions need not be given. They varied quite widely in the proportions of molybdic acid to free nitric acid and ammonium nitrate as well as in degrees of concentration.

Without going into a detailed discussion of the results and the advantages possessed by the different molybdic solutions for different purposes, we will merely state that we found the official molybdic solution of the following formula and made by dissolving 100 grams of molybdic acid in 400 grams, or 417 cc., of ammonia of 0.96 sp. gr., and pouring this into 1250 cc., or 1500 grams nitric acid of 1.20 sp. gr. to be the one best suited to the volumetric method for very small quantities of phosphoric acid, one per cent or less. For percentages larger than one, the foregoing solution with the addition of eighty extra cc. of 1.42 sp. gr. nitric acid, or five cc. to each 100 cc. of official molybdic solution was found to be the best. 100 cc. of this latter solution contains practically six grams of molybdic acid, four and six-tenths grams ammonium nitrate, and thirty-five cc. free nitric acid of 1.42 sp. gr., which is about the largest quantity of free nitric acid in proportion to molybdic acid that can be used in a molybdic solution not to interfere with quick and ready precipitation of phosphoric acid. When a larger proportion of free nitric acid is in the solution, precipitation of phosphoric acid is either incomplete or is very materially retarded. This modified official molybdic solution, containing the large amount of nitric acid, can be readily used for all percentages of phosphoric acid, but it contains rather too much free nitric acid to allow of the quickest precipitation of very small quantities, but by extending the time of precipitation to eight to ten minutes it will be found to be complete even when very small amounts are present. The judgment and manipulation of the analyst will, however, be the best guide as to whether he will employ the solution containing the larger amount of nitric acid for all percentages, or whether he will only use it for those above one or so, and use the regular official solution for less amounts.

EFFECT OF ORGANIC ACIDS IN PREVENTING DEPOSITION OF  
MOLYBDIC ACID.

Jüptner<sup>1</sup> has successfully used two-tenths to six grams of tartaric acid per 100 cc. of molybdic solution for preventing the deposition of molybdic acid in the determination of phosphorus in steel. One to four grams of citric acid to 100 cc. of the two foregoing molybdic solutions were employed in the hope of accomplishing the same object. When three and four grams of citric acid were used precipitation was not complete in fifteen or twenty minutes, and with smaller quantities (one, one and five-tenths, and two grams) precipitation was complete in a reasonable length of time (seven to fifteen minutes), but the results at best showed no advantage over those obtained on the same samples with molybdic solutions without the presence of citric acid.

## ACIDITY OF AMMONIUM PHOSPHOMOLYBDATE.

Hundeshagen<sup>2</sup> has stated that it required twenty-three molecules of  $\text{Na}_2\text{CO}_3$  (or of  $\text{Na}_2\text{O}$ ) to neutralize the ammonium phosphomolybdate containing one molecule of phosphorus pentoxide.

H. Pemberton, Jr.,<sup>3</sup> working upon a solution of chemically pure disodium hydrogen phosphate, found that 23.2 molecules of sodium carbonate were necessary to neutralize the ammonium phosphomolybdate containing one phosphorus pentoxide molecule; a second determination,<sup>4</sup> however, working in the same way, gave him 22.99 molecules.

In the course of my work upon the volumetric method, I have determined the acidity of ammonium phosphomolybdate in two ways. First, by finding the amount of alkali necessary to neutralize the ammonium phosphomolybdate formed from a given amount of phosphate. This was done by dissolving ten grams of chemically pure disodium hydrogen phosphate in a liter of water, carefully measuring out twenty cc. portions, precipitating with molybdic solution, washing thoroughly according to our practice in the volumetric method, and titrating with alkali.

The results obtained are as follows :

<sup>1</sup> Abs. Expt. Sta. Record, 6, 610.

<sup>2</sup> *Ztschr. anal. Chem.*, 28, 141-172.

<sup>3</sup> *This Journal*, 15, 382.

<sup>4</sup> *Ibid.*, 16, 278.

	Cc. of phosphate solution used.	Equaling grams $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .	Equaling grams $\text{P}_2\text{O}_5$ .	Cc. KOH solution required to neutralize phosphomolybdate formed.
1	20	0.20000	0.039652	39.80
2	20	0.20000	0.039652	39.80
3	20	0.20000	0.039652	39.80

Dividing the weight of phosphorus pentoxide by the number of cc. alkali required to neutralize the phosphomolybdate formed, we find that 100 cc. alkali has neutralized an amount of ammonium phosphomolybdate containing 99.628 milligrams phosphorus pentoxide.

The alkali was now titrated against semi-normal hydrochloric acid, carefully standardized by silver nitrate to contain 18.2285 grams hydrochloric acid per liter. 100 cc. of the alkali equaled 64.5 cc. of the semi-normal acid, which contained 1175.74 milligrams hydrochloric acid, which in turn equals 1519.3 milligrams potash, or 2228.6 milligrams potassium carbonate. Therefore, 1519.3 milligrams potash equals 99.628 milligrams phosphorus pentoxide in the yellow precipitate. Dividing each of these by its molecular weight, we obtain

$$\text{for phosphorus pentoxide } \frac{99.628}{142.06} = 0.7013.$$

$$\text{for potash } \frac{1519.3}{94.22} = 16.125.$$

$$\text{Then, } \text{P}_2\text{O}_5 : \text{K}_2\text{O} = 0.7013 : 16.125 = 1 : 22.993.$$

The relation between standard alkali and phosphorus pentoxide in the "yellow precipitate" was now determined by preparing pure phosphomolybdates by precipitating sodium phosphate with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation, first with dilute nitric acid and then with water, and drying at 130° to 150° C. to constant weight. These phosphomolybdates contained 2.232 per cent. nitrogen (average of seven analyses), the theory being 2.238; and 1.645 per cent. phosphorus, the theory being 1.651. The following results were obtained by titrating a portion of three of these :

	Grams ammonium phosphomolybdate used.	Cc. standard alkali required to neutralize.
1	1.2322	46.55
2	0.8050	30.45
3	0.7955	30.10
Total	2.8327	107.10

One hundred cc. of alkali has, therefore, neutralized 2.6449 grams of ammonium phosphomolybdate, which multiplied by 3.783, (the per cent. of phosphorus pentoxide in the "yellow precipitate") gives 100.05 milligrams phosphorus pentoxide in 2.6449 grams of this salt, and which corresponds to 100 cc. of the alkali used.

One hundred cc. of this alkali was found as before to equal 64.74 cc. semi-normal hydrochloric acid, which contains 1180.14 milligrams hydrochloric acid, and which in turn equals 2237.08 milligrams of potassium carbonate. Therefore 2237.08 milligrams potassium carbonate equals the 100.05 milligrams of phosphorus pentoxide contained in the 2.6449 grams of "yellow precipitate."

Dividing by molecular weights, there is found

for phosphorus pentoxide  $\frac{100.05}{142.06} = 0.7042$ .

for potassium carbonate  $\frac{2237.08}{138.22} = 16.185$ .

Therefore,  $P_2O_5 : K_2CO_3 = 0.7042 : 16.185 = 1 : 22.983$ .

It has, therefore, required practically twenty-three molecules of potassium carbonate (or of potash) to neutralize an amount of ammonium phosphomolybdate ( $6NH_4.P_2O_5.24MoO_3$ ) containing one molecule of phosphorus pentoxide. On this basis, one cc. of a standard alkali containing 18.17106 grams of potassium hydroxide to the liter would equal one milligram phosphorus pentoxide. 100 cc. of this solution will neutralize 32.38 cc. of normal acid; and either the acid or alkali to be used in the volumetric method can be made by diluting 323.8 cc. of corresponding normal solution to one liter.

The above calculations are based upon the following atomic weights:

Sodium.....23.05	Oxygen.....16.	Chlorine.....35.45
Hydrogen ... 1.007	Potassium ...39.11	Molybdenum 96.
Phosphorus..31.03	Carbon .....12.	Nitrogen ....14.03

#### RESULTS BY VOLUMETRIC METHOD AS NOW WORKED IN THIS LABORATORY COMPARED WITH GRAVIMETRIC RESULTS.

The writer was again reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1894-95, and the foregoing investigation was made with a view of setting the method in better shape for trial by this



association and for perfecting it, if possible, for use in this laboratory. The method was accordingly changed quite materially, redescribed to accord with results of the preceding work, and sent out to various official and other chemists for trial with three samples upon which to conduct the work. These samples were :

No. 1 was a chemically pure disodium hydrogen phosphate solution containing ten grams of the salt per liter, the theoretical percentage of phosphorus pentoxide in it being 19.826.

No. 2 was solution No. 1 diluted with five parts of water, and therefore contained the equivalent of 3.304 per cent. phosphorus pentoxide in fifty cc.

No. 3 was a mixed fertilizer.

The results obtained in this laboratory on these samples by gravimetric and volumetric methods and presented to the association are brought together in Table II.

These results are what, I deem, may be termed *most excellent*.

It may not be out of place here to state also that the results of nine other chemists on these same samples, including thirty-one determinations on No. 1 and thirty-three on No. 2, excluding three results, are as good as those in the table. Seventy-three per cent. of all the results of thirteen chemists on sample No. 1 are within 0.05 per cent. of the theory, and ninety-three per cent. within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of all results are within 0.05 per cent. of the theory and all are within one-tenth.

This summary of results of members of the Association of Official Agricultural Chemists by the volumetric method are in rather marked contrast to the results of this and all previous years by the official gravimetric method, and also to the results by the volumetric method as worked last year. The results last year by the volumetric method were considered on the whole as encouraging, while the method as worked this year has given extremely good results in all hands.

The volumetric and gravimetric methods have been compared in this laboratory upon quite a variety of phosphates and fertilizer materials of varying percentages. The results follow in Table III.

TABLE II. TOTAL PHOSPHORIC ACID BY GRAVIMETRIC AND VOLUMETRIC METHODS.

Analyst.	Sample No. 1.					Sample No. 2.					Sample No. 3.				
	Methods and washings.					Methods and washings.					Methods and washings.				
	Official Gravimetric.	Volumetric.	Washing Water.	Difference + greater - less than gravimetric.	Per cent.	Official Gravimetric.	Volumetric.	Washing Water.	Difference + greater - less than gravimetric.	Per cent.	Official Gravimetric.	Volumetric.	Washing Water.	Difference + greater - less than gravimetric.	Per cent.
W. M. Allen .....	Per cent.	Per cent.	cc.	Per cent.		Per cent.	Per cent.	cc.	Per cent.		Per cent.	Per cent.	cc.	Per cent.	
	19.93	19.81	275	— .11		3.38	3.28	265			12.50	12.32	275		
	19.97	19.84	250			3.39	3.27	300			12.59	12.39	300		
	19.96	19.88	285			....	3.27	275	— .109		....	12.39	350	— .17	
C. B. Williams .....	....	....	....			....	3.29	275			....	....	....		
	....	....	....			....	3.28	300			....	....	....		
	....	....	....			....	3.27	275			....	....	....		
	19.91	19.80	220			....	3.32	210			....	12.32	240		
F. B. Carpenter .....	....	19.85	230	— .073		....	3.32	220			....	12.32	270		
	....	19.85	250			....	3.32	205			....	12.32	235		
	....	19.85	250			....	3.32	220			....	12.42	220		
	19.83	19.85	275	+ .03		3.38	3.32	250	— .006		12.43	12.39	250	+ .0	
B. W. Kilgore.....	....	19.87	275			3.33	3.34	250			12.37	12.43	250		
	19.96	19.83	280			3.38	3.32	300			....	12.40	225		
	19.89	19.83	280	— .12		3.39	3.31	200	— .083		....	12.40	190		
	20.00	19.83	250			3.40	3.30	200			....	12.37	200		
Average.....	....	....	....			....	3.30	210			....	12.37	250		
Theory .....	19.93	19.84	....			3.38	3.302	....			12.475	12.37	....		
Variation of lowest result from theory .....	19.826	19.826	....			3.304	3.304	....			....	....	....		
Variation of highest result from theory .....	0.004	0.026	....			0.026	0.034	....			....	....	....		
	0.174	0.054	....			0.096	0.034	....			....	....	....		

TABLE III. DETERMINATIONS OF PHOSPHORIC ACID IN VARIOUS MATERIALS BY VOLUMETRIC AND GRAVIMETRIC METHODS.

Material.	Number.	Gravimetric Method.	Volumetric method.	Washing water.	Difference greater + less — than gravi-metric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washing water.	Difference greater + less — than gravi-metric method.
C. B. Williams, Analyst.....											
Cottonseed meal	1	Per cent. 0.08	Per cent. 0.08	cc. 130	Per cent. .00		16	Per cent. 9.54	Per cent. 9.45	cc. 260	Per cent. .09
	2	0.37	0.35	160	.02		17	10.72	10.65	270	+0.07
	3	1.32	1.28	100	.04		18	6.46	6.40	230	+0.06
	4	1.50	1.45	240	.05		19	6.55	6.60	250	+0.05
	5	0.88	0.79	215	.09		20	5.45	5.50	290	+0.05
	6	0.65	0.61	250	.04	Fertilizers and fertilizing ma- terials	21	6.52	6.60	280	+0.08
	7	0.64	0.61	250	.03		22	7.47	7.44	250	+0.03
	8	1.27	1.25	240	.02		23	7.42	7.44	230	+0.02
	9	1.29	1.25	250	.04		24	7.42	7.48	240	+0.04
	10	4.96	4.95	155	.01		25	17.55	17.52	260	.03
	11	4.98	4.92	180	.06		26	17.55	17.52	260	.03
	12	11.80	11.80	130	.00	Florida phosphate	27	37.84	37.80	260	.04
	13	11.88	11.45	250	.13		28	13.12	13.15	260	.03
	14	9.77	9.80	240	.01	Acid phosphate	29	15.49	15.35	290	.14
	15	10.04	10.05	220	.01		30	13.27	13.15	280	.12
W. M. Allen, Analyst.....											
Mixed fertilizer	1	11.58	11.45	250	.09	Acid phosphate	3	15.49	15.47	250	.04
"	"	11.53	11.53	280	.02	Mixed fertilizer	4	10.72	10.70	275	.03
"	2	9.54	9.53	285	.02		5	10.72	10.67	275	.05
B. W. Kilgore, Analyst.....											
Mixed fertilizer	1	9.77	9.76	275	.00	Mixed fertilizer	11	10.72	10.68	275	.04
"	2	9.75	8.96	210	.07	Acid phosphate	12	13.27	13.21	275	.06
"	3	10.67	10.66	220	.01	Mixed fertilizer	13	11.71	11.63	275	.08
"	4	11.58	11.60	275	.02	"	14	11.88	11.78	275	.13
"	5	9.77	9.76	275	.01	"	15	9.43	9.38	280	.05
"	6	10.04	10.01	275	.03	Bone meal	16	9.71	9.80	230	+0.09
"	7	9.54	9.48	275	.06	"	17	10.38	10.30	280	+0.08
Acid phosphate	8	15.40	15.42	275	.03	Acid phosphate	18	20.53	20.48	210	.05
Insoluble	9	2.57	2.60	230	.07		19	15.03	15.10	220	+0.08
Reporter's sample No. 1	10	19.88	19.88	260	.05	Reporter's sample No. 2 <sup>a</sup>	20	3.38	3.30	220	.08
		19.86		260		Reporter's sample No. 3	21	3.39	3.43	260	
		19.89		260				12.43	12.43	260	
								13.45	13.45	260	

These volumetric results show close agreement with the gravimetric ones, though they are generally slightly lower than the latter. When we observe the close agreement of duplicate results by the volumetric method and remember the tendency of the molybdate method to give high results, we have ground for believing that the volumetric results are more nearly correct.

#### RESULTS ON A HIGH GRADE PHOSPHATE.

To see how the volumetric method would work on a very high percentage phosphate and to see how the results by the two methods would compare on it, a high grade Florida phosphate was submitted to analysis, with the following results :

	C. B. Williams, analyst. per cent.	B. W. Kilgore, analyst. per cent.
Gravimetric method.....	38.12	
Volumetric method .....	37.80 37.84	37.80 37.88
Less by volumetric method.....	0.30	

The foregoing results by the volumetric method, our work upon it, and experience with it generally lead us to consider it a more accurate and reliable method than the molybdate-magnesia method. Since the change of temperature of precipitation, precipitating reagent, wash solutions, and manner of washing from what they were in the Pemberton method, the difficulty of getting occasionally very high results in the midst of good ones, and which did so much to destroy faith in the method, seems not to occur under the new method of procedure. The accuracy, reliability and rapidity of the method, a man being able to make, we think, twice as many determinations by it as by the gravimetric method, causes us to feel that the large amount of time which we have put upon the method has been well spent and will soon repay us in the saving of time on this class of work in our own laboratory, to say nothing of the service it may be to others having, as we do, large amounts of phosphoric acid work to do.

I am indebted to Messrs. C. B. Williams and W. M. Allen for assistance in carrying out the foregoing work.

The method, as we have found it to give the best results, may be described as follows :

Weigh two grams of substance and make solution by one of the following methods: (1) Evaporate with five cc. of magnesium nitrate solution, ignite, and dissolve in hydrochloric acid. This is for organic materials. (2) Dissolve in thirty cc. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add thirty cc. concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about five-tenths gram of finely pulverized potassium chlorate. These (2 and 3) are for ordinary phosphates and fertilizers. (4) Dissolve in fifteen to thirty cc. of strong hydrochloric acid and five to ten cc. of nitric. This is for phosphates containing much iron and aluminum. Method 2 is preferred when these acids are a suitable solvent for the material. Make up to 200 cc. (or any other convenient volume), measure out twenty cc. for totals, or for percentages above five or six; and forty cc. for insolubles, or for percentages below five or six, corresponding to two-tenths and four-tenths gram substance respectively, add about five cc. concentrated nitric acid, when method 2 for solution has been used and about ten cc. when method 1, 3, or 4 has been used. Now add ammonia until precipitate just begins to form, dilute high percentage solutions to about 100 cc., and low percentage ones to from sixty to seventy-five cc., digest in water-bath at 60° to 65° C., and after filtering the molybdic solution to be used in this method, precipitate, not using any greater excess of molybdic solution than is necessary to insure complete precipitation; let stand in bath six minutes from the time the molybdate is added, and filter as quickly as possible upon a three-inch Hirsch funnel, whose perforations are covered with a disk of soft filter-paper, or in a Gooch crucible with one or two pieces of filter-paper slightly larger than the bottom of the crucible, tightly pressed against the bottom of the crucible, or upon a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos; using the pump in all cases. Filter-paper may be used, but the other filters in the order named are much to be preferred.

It is *especially urged* that the three-inch Hirsch funnel be used where possible, as it permits of rapid filtration and easy and thorough washing. Wash the precipitate twice by decantation

with dilute nitric acid, using fifty to seventy-five cc. each time and agitating thoroughly, once by decantation with the same amount of three per cent. potassium or ammonium nitrate solution, then on the filter and with 200 to 500 cc. water, (250 cc. is usually enough) or until no longer acid. Now wash the precipitate with filter back into the beaker, titrate with potassium hydroxide, and back with nitric acid, using phenolphthalein as indicator and adding acid until color disappears.

In washing by decantation, if the precipitate is allowed to settle completely each time, no trouble will be experienced in the after washing.

Where the phosphoric acid is below one per cent., the precipitation is not so rapid as in larger percentages and may require eight or even ten minutes to be complete.

#### REAGENTS TO BE USED IN THE VOLUMETRIC METHOD.

*Molybdic Solution.*—Dissolve 100 grams of molybdic acid in 400 grams, or 417 cc. of ammonia, sp. gr. 0.96, and pour the solution thus obtained into 1500 grams, or 1250 cc. of nitric acid, sp. gr. 1.20, and add eighty cc. nitric acid, sp. gr. 1.42. Or to each 100 cc. of the official molybdic solution (the above formula without the eighty cc. nitric acid), add five cc. 1.42 sp. gr. nitric acid. This solution should be filtered each time before using.

*Dilute Nitric Acid Wash.*—Dilute 100 cc. 1.42 sp. gr. nitric acid to one liter.

*Potassium or Ammonium Nitrate Wash.*—Dissolve three grams of either in 100 cc. of water.

*Alcoholic Solution of Phenolphthalein.*—100 cc. to one gram.

*Standard Potassium Hydroxide.*—This solution should contain 18.17106 grams potassium hydroxide to the liter. One cc. of this solution equals one milligram phosphorus pentoxide (one per cent. phosphorus pentoxide on basis of one-tenth gram substance) 100 cc. of it will neutralize 32.38 cc. normal acid, and can be made by diluting 323.81 cc. of normal potassium hydroxide, which has been freed from carbonates by barium hydroxide to one liter.

*Standard Nitric Acid* of same, or one-half, the strength of alkali. Hydrochloric or sulphuric acid will do.

# THE RELATIONSHIP OF THE HEAT OF VAPORIZATION OF GASES TO THEIR DENSITY AND ALSO TO THEIR BOILING-POINT.

By WM. L. DUDLEY.

Received September 27, 1895.

IN studying the heat of vaporization or latent heat of various gases it soon became apparent that this constant bore an interesting relationship to their density and boiling-point. To trace out this relationship I have endeavored to obtain the latest and best latent heat determinations, as well as the specific gravity of the liquids at the boiling-point. Accurate data of this kind are scarce, and there are few homologous series in which these constants have been determined for many members. However, I have obtained a sufficient number of trustworthy determinations to show some results, which seem to be worth recording.

The amount of heat absorbed by one cc. of vapor (reduced to 0° and 760 mm. pressure) in the passage of the liquid to the gaseous state, is taken as the standard for comparison. This constant is found by the formula

$$L = \frac{H \times w}{W}.$$

where  $L$  = the heat of vaporization in one cc. of vapor,

$W$  = the weight of one cc. of the liquid at its boiling-point,

$H$  = the heat of vaporization,

and  $w$  = the weight of one cc. of the vapor at 0° and 760 mm. pressure.

Until the latent heat researches made by R. Schiff<sup>1</sup> these constants were determined without any special reference to the relationship of the compounds to one another, and, therefore, not many series can be found complete enough to make a comparison. I believe, however, that I have gathered the data quite completely and I give in this paper all the series in which the data are complete for as many as three members.

In the following tables the columns marked

<sup>1</sup> *Ann. Chem.* (Liebig), 234, 338, 1886.

D = the vapor density,

B. P. = Boiling-point in absolute temperature,

S. G. = Specific gravity at the boiling-point,

H. V. = Heat of vaporization in calories,

V = Volume of vapor, in cubic centimeters (reduced to 0° and 760 mm. pressure), produced from one cc. of liquid at the boiling-point.

L = Heat of vaporization in a unit of volume (one cc.) of gas reduced to 0° and 760 mm. pressure.

The specific gravity of liquids at the boiling-point is taken from Clarke's tables of "Constants of Nature," where the references are fully given. The boiling-point is obtained from Carnelley's tables.

I will first show the results obtained from some of the fatty acids and their alkyl compounds.

Name.	Formula.	FORMATES.					
		D.	B. P.	S. G.	H. V.	V.	L.
Formic acid	HCHO <sub>2</sub>	23	373.8°	1.1175	120.72 <sup>1</sup>	542.26	0.2226
Methyl formate	CH <sub>3</sub> CHO <sub>2</sub>	30	305.3°	0.95196	117.10 <sup>2</sup> 102.70 <sup>3</sup>	354.15	0.3306 0.2900
Ethyl formate	C <sub>2</sub> H <sub>5</sub> CHO <sub>2</sub>	37	326.5°	0.86667	92.15 <sup>4</sup>	263.36	0.3499
Propyl formate	C <sub>3</sub> H <sub>7</sub> CHO <sub>2</sub>	44	354.2°	0.82146	85.25 <sup>4</sup>	208.37	0.4091
Isobutyl formate	C <sub>4</sub> H <sub>9</sub> CHO <sub>2</sub>	51	371.0°	0.7784	77.0 <sup>4</sup>	170.34	0.4520
Isoamyl formate	C <sub>5</sub> H <sub>11</sub> CHO <sub>2</sub>	58	397.0°	0.7554	71.65 <sup>4</sup>	145.35	0.4929

Fig. 1 represents the curves of the formates, the density and boiling-point curves being shown on the same sheet. In all cases the corresponding acids fall in line in the density curves but not in the boiling-point curves. The acids, however, form both density and boiling-point curves of their own, as will be shown later on.

It will be seen from Fig. 1 that the heat of vaporization per unit of volume (H. V.) of methyl formate obtained from the result of Andrews' determination is too high. To conform to the curve it should be 0.2900 which would give 102.70 as the heat of vaporization (H. V.) instead of 117.10 as given by Andrews, whose determination has never been verified. But

<sup>1</sup> Favre and Silbermann : *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Andrews : *Chem. Soc. Quar. J.*, 1, 27.

<sup>3</sup> Calculated from the data furnished by the curves shown in this paper.

<sup>4</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.



# HEAT OF VAPORIZATION.

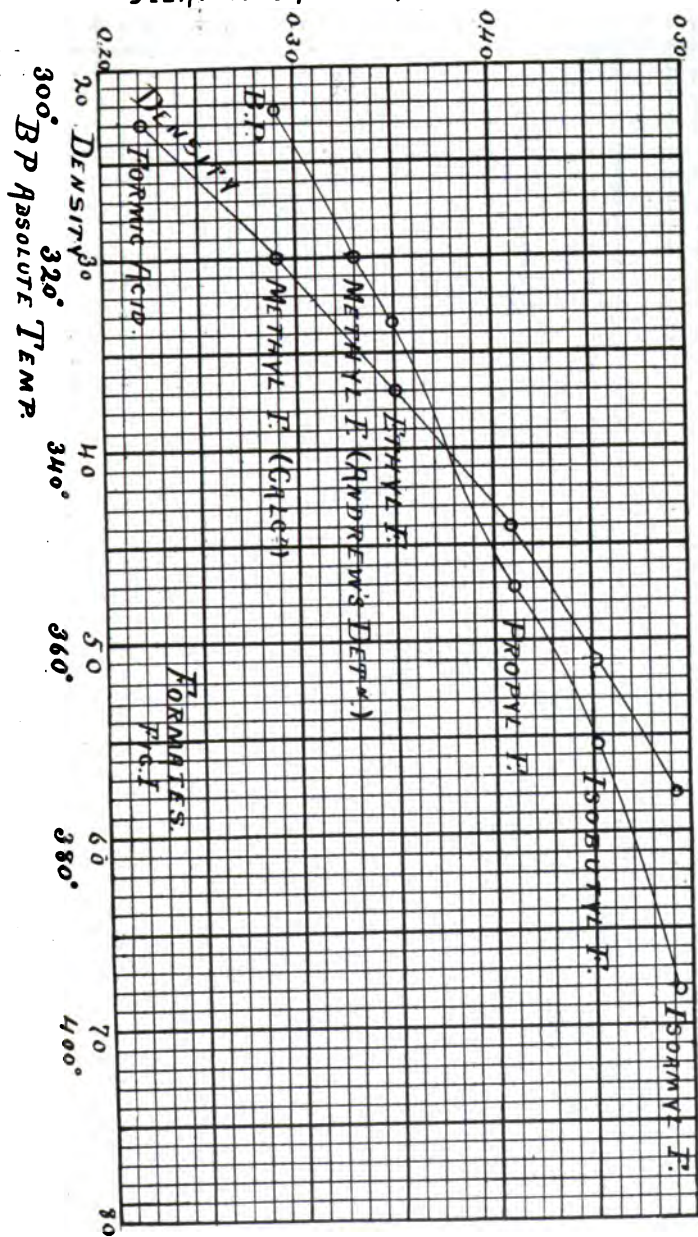


FIG. 1.

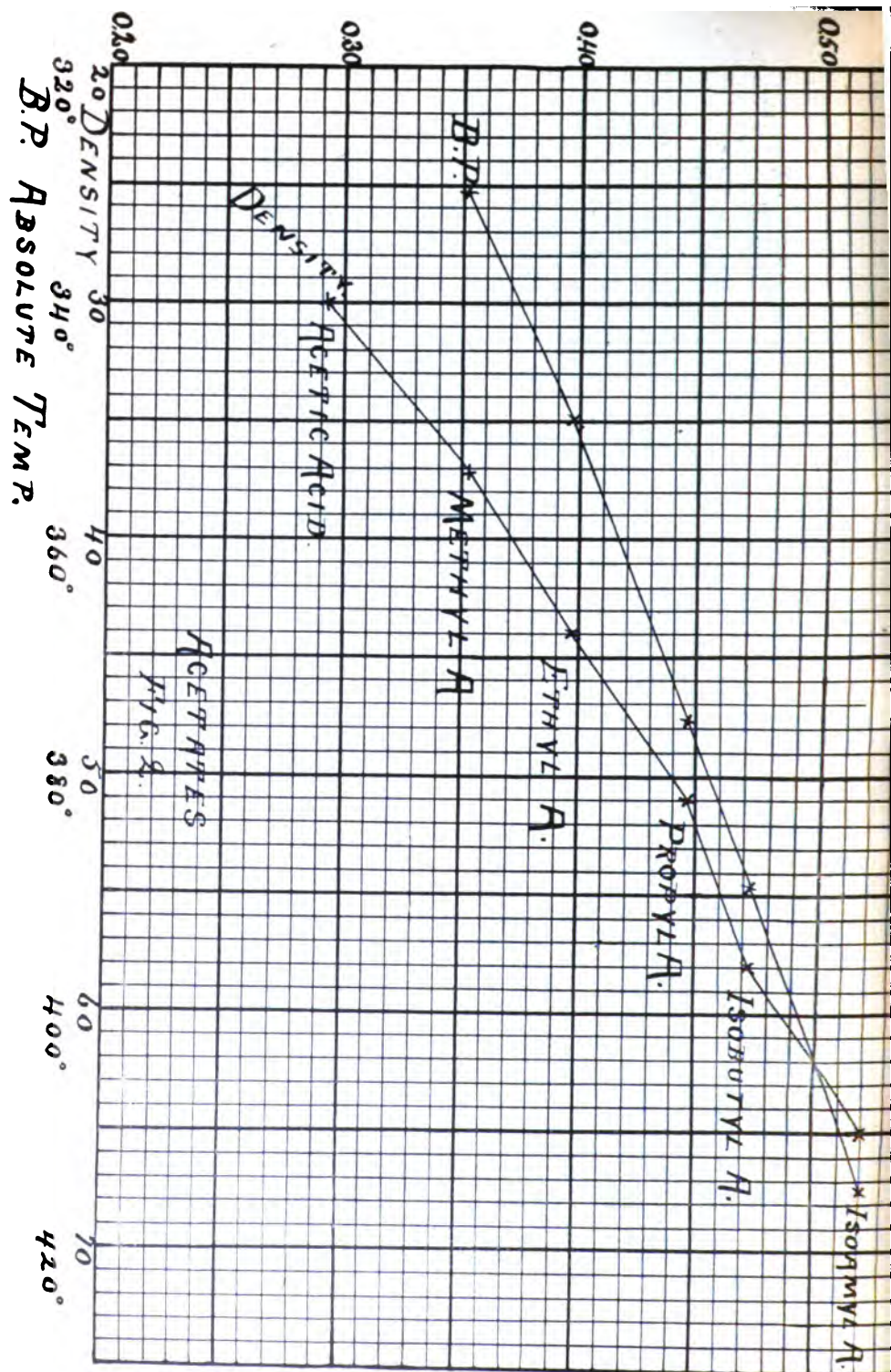


FIG. 2.

since many of Andrews' determinations have been found by later investigators to be considerably too high, it is reasonable to suppose under the circumstances that this one is too high also. To substantiate this I will give the following instances, which may be cited from determinations made by Andrews and Schiff :

Methyl acetate	{ Andrews,	110.20
	{ Schiff,	93.90-94.0
Ethyl acetate	{ Andrews,	92.68
	{ Schiff,	83.0-83.1-83.1
Ethyl formate	{ Andrews,	105.30
	{ Schiff,	92.2-92.1

## ACETATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	30	391.1°	0.9372	101.91 <sup>1</sup>	348.66	0.2923
Methyl acetate	$\text{CH}_3\text{C}_2\text{H}_3\text{O}_2$	37	330.3°	0.8808	93.95 <sup>2</sup>	265.68	0.3536
Ethyl acetate	$\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$	44	350.0°	0.82673	83.1 <sup>2</sup>	209.70	0.3961
Propyl acetate	$\text{C}_3\text{H}_7\text{C}_2\text{H}_3\text{O}_2$	51	375.3°	0.7917	77.3 <sup>2</sup>	173.25	0.4462
Isobutyl acetate	$\text{C}_4\text{H}_9\text{C}_2\text{H}_3\text{O}_2$	58	389.8°	0.7708	69.9 <sup>2</sup>	148.32	0.4713
Isoamyl acetate	$\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$	65	415.0°	0.74295	66.35 <sup>2</sup>	127.56	0.5201

The acetates form very good curves, as will be seen in Fig. 2. The boiling-point curve is almost a straight line. It has been shown above that Schiff's determinations of the heats of vaporization (H. V.) of methyl and ethyl acetates are much lower than those of Andrews. Favre and Silberman's determination gives a number for ethyl acetate much higher than that of either of the other investigators, it being 105.8. The results of Schiff are taken as being more nearly correct.

## PROPIONATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Propionic acid	$\text{H.C}_3\text{H}_5\text{O}_2$	37	413.7°	0.8589	90.42 <sup>3</sup>	259.08	0.3490
Methyl propionate	$\text{CH}_3\text{C}_3\text{H}_5\text{O}_2$	44	353.0°	0.836798	84.15 <sup>4</sup>	212.25	0.3965
Ethyl	$\text{C}_2\text{H}_5\text{C}_3\text{H}_5\text{O}_2$	51	371.7°	0.7962	77.1 <sup>4</sup>	174.64	0.4415
Propyl	$\text{C}_3\text{H}_7\text{C}_3\text{H}_5\text{O}_2$	58	395.6°	0.76815	71.5 <sup>4</sup>	147.81	0.4832
Isobutyl	$\text{C}_4\text{H}_9\text{C}_3\text{H}_5\text{O}_2$	65	409.8°	0.74424	66.0 <sup>4</sup>	127.78	0.5165
Isoamyl	$\text{C}_5\text{H}_{11}\text{C}_3\text{H}_5\text{O}_2$	72	433.5°	0.7295	63.05 <sup>4</sup>	113.08	0.5576

The curves representing the propionates are shown in Fig. 3, and it will be seen that they are quite regular. The heat of vaporization (H. V.) of propionic acid has never been deter-

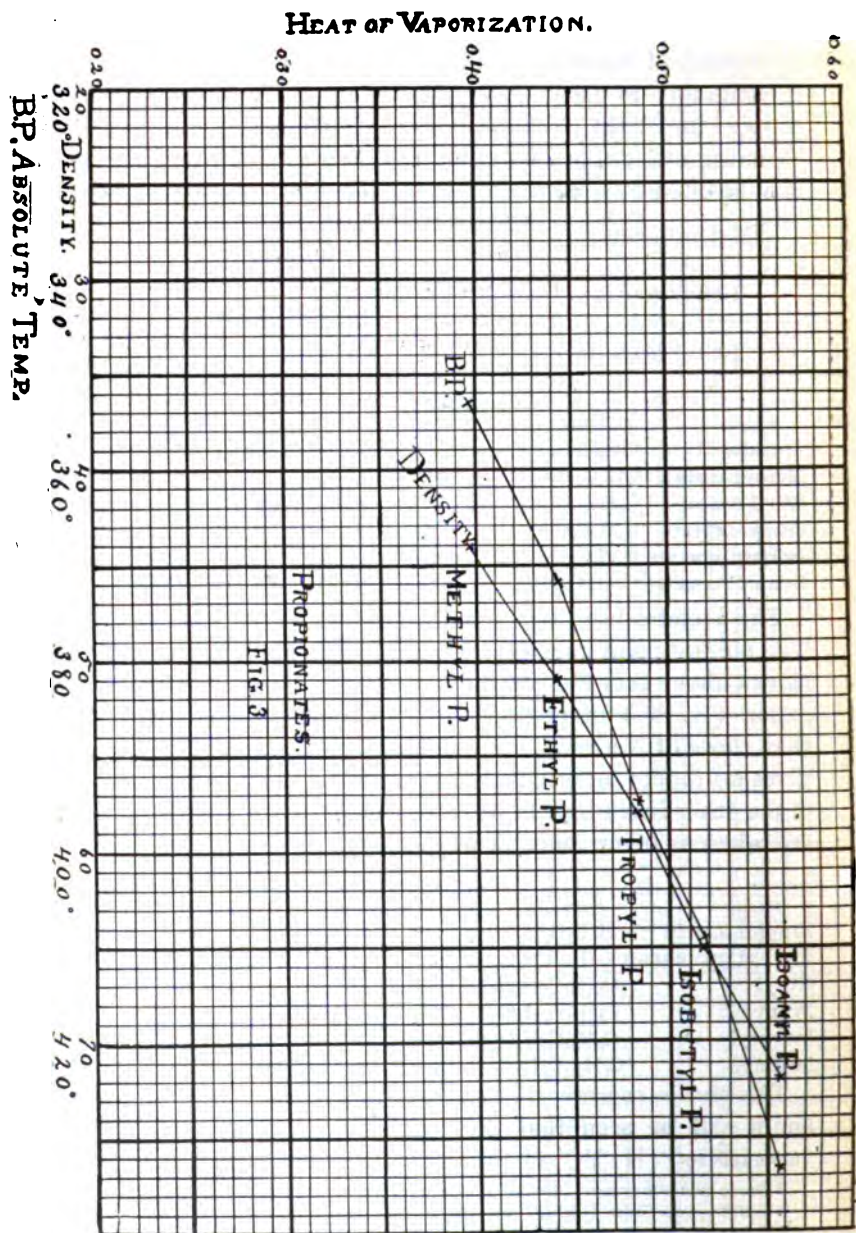
<sup>1</sup> Favre and Silberman : *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.

<sup>3</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>4</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.





**FIG. 3.**

mined ; but according to the density curve of the propionates, its heat per unit of volume of vapor (L.) should be 0.3490, which would give for the heat of vaporization (H. V.) the number 90.42.

BUTYRATES.							
Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Butyric acid	$\text{H.C}_4\text{H}_7\text{O}_2$	44	435.5°	0.8120	114.67 <sup>1</sup> 82.79 <sup>2</sup>	205.96	0.5567 0.4020
Methyl butyrates	$\text{CH}_3\text{C}_4\text{H}_7\text{O}_2$	51	375.3°	0.80261	87.93 <sup>1</sup> 77.25 <sup>2</sup>	175.64	0.4972 0.4398
Ethyl "	$\text{C}_2\text{H}_5\text{C}_4\text{H}_7\text{O}_2$	58	392.0°	0.7694	71.5 <sup>3</sup>	148.05	0.4829
Propyl "	$\text{C}_3\text{H}_7\text{C}_4\text{H}_7\text{O}_2$	65	416.4°	0.745694	66.2 <sup>3</sup>	128.03	0.5170
Isobutyl "	$\text{C}_4\text{H}_9\text{C}_4\text{H}_7\text{O}_2$	72	429.7°	0.7163	61.9 <sup>3</sup>	111.03	0.5575
Isoamyl "	$\text{C}_5\text{H}_{11}\text{C}_4\text{H}_7\text{O}_2$	79	451.0°	0.71148	59.4 <sup>3</sup>	100.51	0.5910

The curves of the butyrates are shown in Fig. 4. The density curve is almost a straight line, while the boiling-point curve breaks badly at propyl butyrate. This would indicate that its boiling-point, as determined, is too high and should be 408° (absolute temperature) instead of 416.4°, as determined by Linneman, which is given the preference by Carnelley over other determinations. The recorded results of the determinations of the boiling-point of propyl butyrate are as follows :

144.3° C.	Pawlewski.
143.42° C.	Linneman.
142.7° C.	Elsässer.
139°-141° C.	Chancel.
137.25° (765)	Pierre and Puchot.

The last result would agree very well with that deduced from the curve, *viz.*, 135° C.

The heat of vaporization (H. V.) of butyric acid has only been determined by Favre and Silberman. Their result is 114.67 cal., which is probably too high. It gives the heat per unit of volume (L.) 0.5567, which throws it entirely out of the curve shown in Fig. 4, according to which the number should be about 0.4020; this would give 82.79 cal. as the heat of vaporization (H. V.) of butyric acid. As will be seen in the table above Favre and Silberman's result for methyl butyrate is much higher than Schiff's.

<sup>1</sup> Favre and Silberman : *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>3</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.

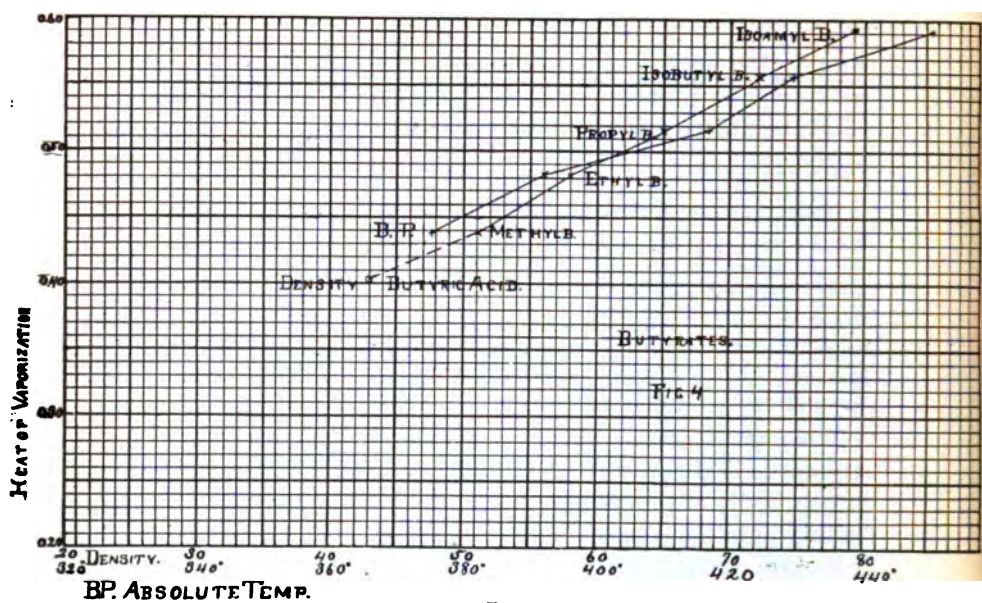


FIG. 4.

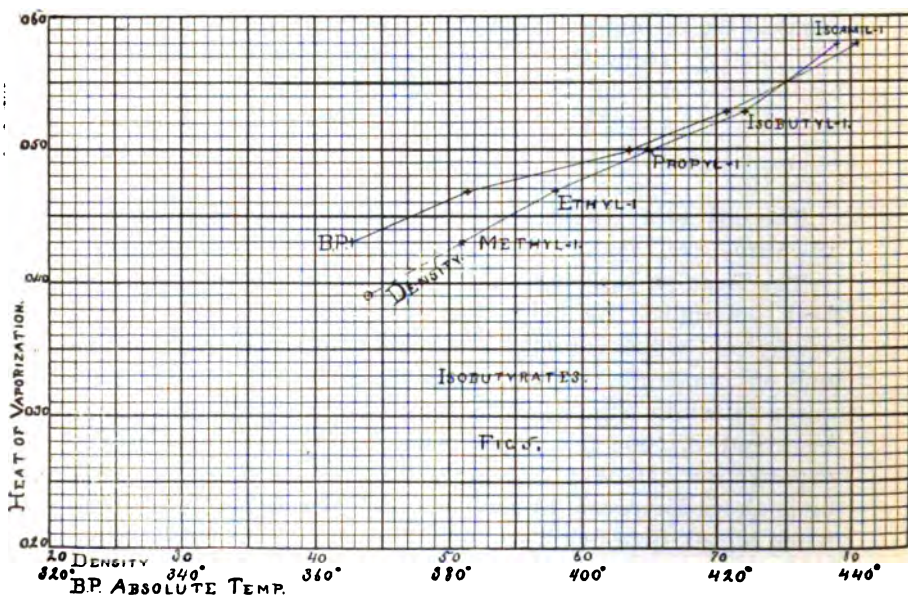


FIG. 5.

## ISOBUTYRATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Isobutyric acid	$\text{H.C}_4\text{H}_7\text{O}_2$	44	428.5°	0.8054	76.67 <sup>1</sup>	204.29	0.3900
Methyl isobutyrate	$\text{CH}_3.\text{C}_4\text{H}_7\text{O}_2$	51	365.5°	0.80397	75.5 <sup>2</sup>	175.93	0.4291
Ethyl "	$\text{C}_2\text{H}_5.\text{C}_4\text{H}_7\text{O}_2$	58	383.0°	0.7681	69.2 <sup>3</sup>	147.80	0.4682
Propyl "	$\text{C}_3\text{H}_7.\text{C}_4\text{H}_7\text{O}_2$	65	407.0°	0.74647	63.9 <sup>2</sup>	128.17	0.4985
Isobutyl "	$\text{C}_4\text{H}_9.\text{C}_4\text{H}_7\text{O}_2$	72	421.6°	0.73281	59.95 <sup>3</sup>	113.59	0.5278
Isoamyl "	$\text{C}_5\text{H}_{11}.\text{C}_4\text{H}_7\text{O}_2$	79	441.0°	0.70662	57.65 <sup>4</sup>	99.82	0.5775

The isobutyrate curves (Fig. 5) seem to indicate that the heats of vaporization (H. V.) of the propyl and isobutyl isobutyric rates as determined are a trifle too low. From the density curve it will be seen that the heat per unit of volume (L.) of isobutyric acid should be 0.3900 which would give 76.67 cal. for the heat of vaporization (H. V.). No determination of this constant has been recorded.

## VALERATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Valeric acid	$\text{H.C}_5\text{H}_9\text{O}_2$	51	458.4°	0.7828	103.52 <sup>2</sup> 73.83 <sup>4</sup>	171.30	0.6042 0.4310
Methyl valerate	$\text{CH}_3.\text{C}_5\text{H}_9\text{O}_2$	58	389.3°	0.77518	69.95 <sup>5</sup>	149.16	0.4684
Ethyl "	$\text{C}_2\text{H}_5.\text{C}_5\text{H}_9\text{O}_2$	65	407.0°	0.74764	64.65 <sup>5</sup>	128.37	0.5036
Propyl "	$\text{C}_3\text{H}_7.\text{C}_5\text{H}_9\text{O}_2$	72	428.5°	0.727405	61.2 <sup>5</sup>	112.75	0.5427
Isobutyl "	$\text{C}_4\text{H}_9.\text{C}_5\text{H}_9\text{O}_2$	79	442.0°	0.70549	57.85 <sup>5</sup>	99.66	0.5805
Isoamyl "	$\text{C}_5\text{H}_{11}.\text{C}_5\text{H}_9\text{O}_2$	86	460.5°	0.698435	56.2 <sup>5</sup>	90.64	0.6200

The curves representing the valerates are shown in Fig. 6. The density curve is quite uniform. Schiff finds the heat of vaporization (H. V.) of isoamyl valerate to be 56.2 cal. and from the curve it will be seen that the heat per unit of volume (L.) should be 0.6200, but this constant could not be calculated since no determination of the specific gravity of this compound at its boiling-point has been made. However, assuming the curve to be correct, the specific gravity at the boiling-point becomes 0.698435. The only determination of the heat of vaporization (H. V.) of valeric acid on record is that of Favre and Silberman, which places it at 103.52 cal. This would give 0.6042 as the heat per unit of volume (L.), while according to the curve it should be 0.4310, which gives 73.83 cal. as the heat of vaporization (H. V.).

<sup>1</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>2</sup> Schiff: *Ann. Chem.* (Liebig), 234, 238.

<sup>3</sup> Favre and Silberman: *Ann. chim. phys.* [3], 37, 464-470.

<sup>4</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>5</sup> Schiff: *Ann. Chem.* (Liebig), 234, 338.



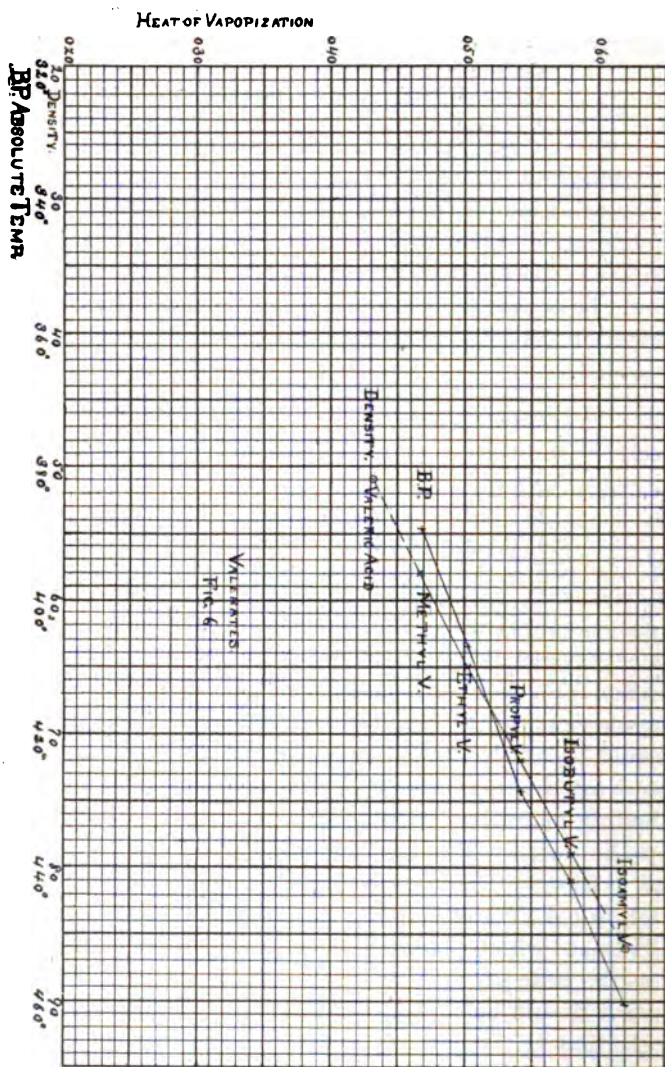


FIG. 6.



According to the boiling-point curve the boiling-point of propyl valerate  $428.5^{\circ}$  (absolute temperature) or  $155.5^{\circ}\text{C}$ . is a trifle too high.

Fig. 7 gives all of the density curves of the compounds above mentioned, in one diagram, showing that the relationship between them is very close and that the uniformity of the curves is very striking.

Fig. 8 is a similar combination of the boiling-point curves, showing the general tread of them to be almost that of a straight line.

## ACIDS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Formic	$\text{H.CHO}_2$	23	$373.8^{\circ}$	1.1175	$92.71^1$ $120.72^2$	542.26	0.2659 0.2226
Acetic	$\text{H.C}_2\text{H}_3\text{O}_2$	30	$391.1^{\circ}$	0.9372	$101.91^3$	348.66	0.2923
Propionic	$\text{H.C}_3\text{H}_5\text{O}_2$	37	$413.7^{\circ}$	0.8589	$90.42^3$	259.08	0.3490
Isobutyric	$\text{H.C}_4\text{H}_7\text{O}_2$	44	$428.5^{\circ}$	0.8054	$79.67^3$	204.29	0.3900
Butyric	$\text{H.C}_4\text{H}_7\text{O}_2$	44	$435.5^{\circ}$	0.8120	$82.79^3$	205.96	0.4020
Valeric	$\text{H.C}_5\text{H}_9\text{O}_2$	51	$458.4^{\circ}$	0.7828	$73.83^3$	171.30	0.4310

The curves of the acids (Fig. 9) are constructed as far as possible from their constants, as determined and recorded by the various observers, but otherwise the data used have been derived from the curves formed by their corresponding compounds.

The heat of vaporization (H. V.) of acetic acid as determined by Ramsey and Young seems to be too low as it does not conform to either the density or boiling-point curve.

## ALCOHOLS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Water	$\text{H.OH}$	9	$373.0^{\circ}$	0.9589	$536.0^4$	1189.11	0.4507
Methyl alcohol	$\text{CH}_3\text{OH}$	16	$339.2^{\circ}$	0.7483	$263.86^5$	521.97	0.5055
Ethyl "	$\text{C}_2\text{H}_5\text{OH}$	23	$351.3^{\circ}$	0.74035	$201.42^5$	359.25	0.5607
Isopropyl "	$\text{C}_3\text{H}_7\text{OH}$	30	$355.8^{\circ}$	0.7413	$159.72^5$	275.78	0.5791
Propyl " (nor.)	$\text{C}_3\text{H}_7\text{OH}$	30	$370.1^{\circ}$	0.7366	$164.07^5$	274.03	0.5987
Isobutyl "	$\text{C}_4\text{H}_9\text{OH}$	37	$381.4^{\circ}$	0.7265	$136.16^5$	219.14	0.6213
Butyl " (nor.)	$\text{C}_4\text{H}_9\text{OH}$	37	$389.96^{\circ}$	0.7269	$138.18^5$	219.26	0.6298
Amyl "	$\text{C}_5\text{H}_{11}\text{OH}$	44	$404.4^{\circ}$	0.7154	$118.15^5$	181.46	0.6511

<sup>1</sup> Ramsey and Young: *J. Chem. Soc.*, Lond., 49, 790.

<sup>2</sup> Favre and Silbermann: *Ann. chim. phys.* [3], 37, 464-470.

<sup>3</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>4</sup> Regnault: *Mem. Acad. Sci.*, 21, 638.

<sup>5</sup> Louguinine: *Compt. rend.*, 119, 601.

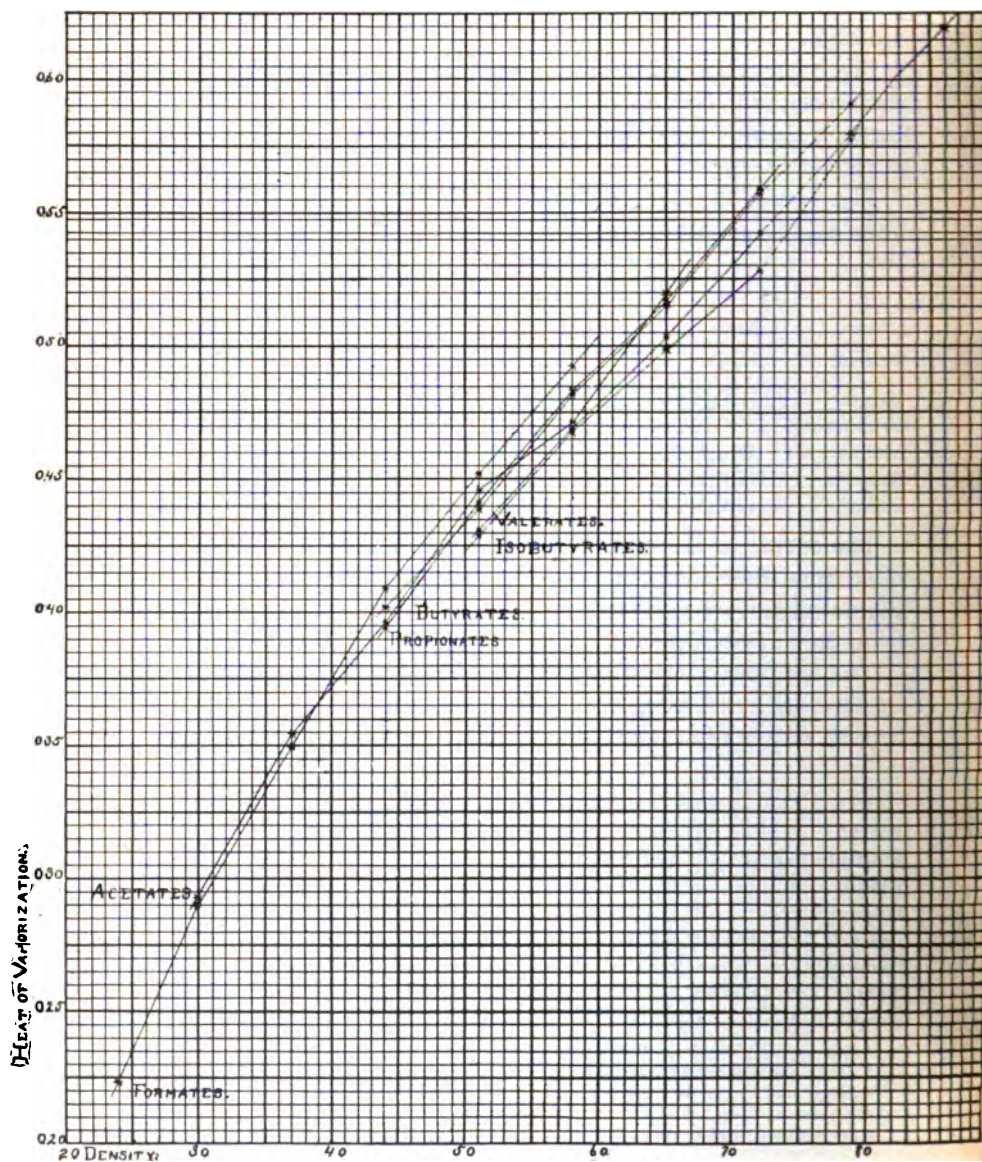


FIG. 7.



**FIG. 8.**

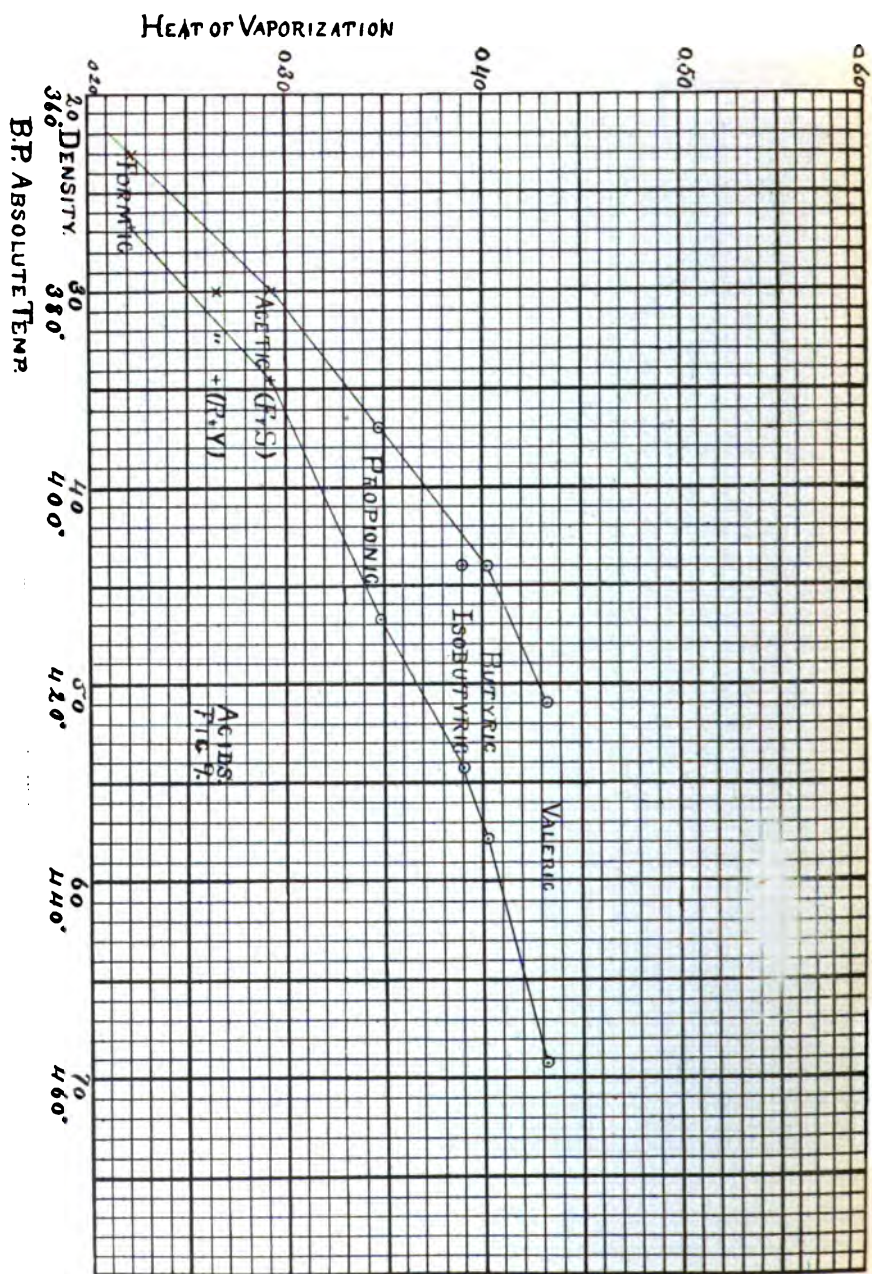


FIG. 9.



The normal alcohols form quite symmetrical curves, as is shown in Fig. 10. In the density curve, water, as the type, falls in with the alcohols as the acids do with their corresponding compounds. It will be noticed that isopropyl and isoamyl alcohols do not fall into line with the normal alcohols, but, as might be expected, they form a portion of a curve for which the data relating to the remaining members of the series are not to be had at present.

In constructing the alcohol curves, the heat of vaporization (H. V.) of methyl alcohol, as determined by Favre and Silberman, was taken in preference to that of Diakonoff, which is believed to be an impossible value. These determinations are as follows:

Favre and Silberman.....	263.86 cal.
Diakonoff.....	123.79 "

In the case of ethyl alcohol the determination of Longuinine was used, although three determinations are recorded as follows:

Favre and Silberman.....	208.92 cal.
Andrews.....	202.40 "
Longuinine.....	201.42 "

Of the two determinations of propyl alcohol (normal)

Diakonoff.....	165.92 cal.
Longuinine.....	164.07 "

I have made use of the latter.

Two determinations of amyl alcohol (by fermentation) are recorded, *viz.*:

Favre and Silberman.....	121.37 cal.
Longuinine.....	118.15 "

and I have used the latter.

The determinations of the other alcohols given in the above table have been made only by Longuinine.

#### HYDROCARBONS.

Sufficient data has been found to make it possible to construct curves for a portion of the  $C_nH_{n-6}$  series of the hydrocarbons, as follows:

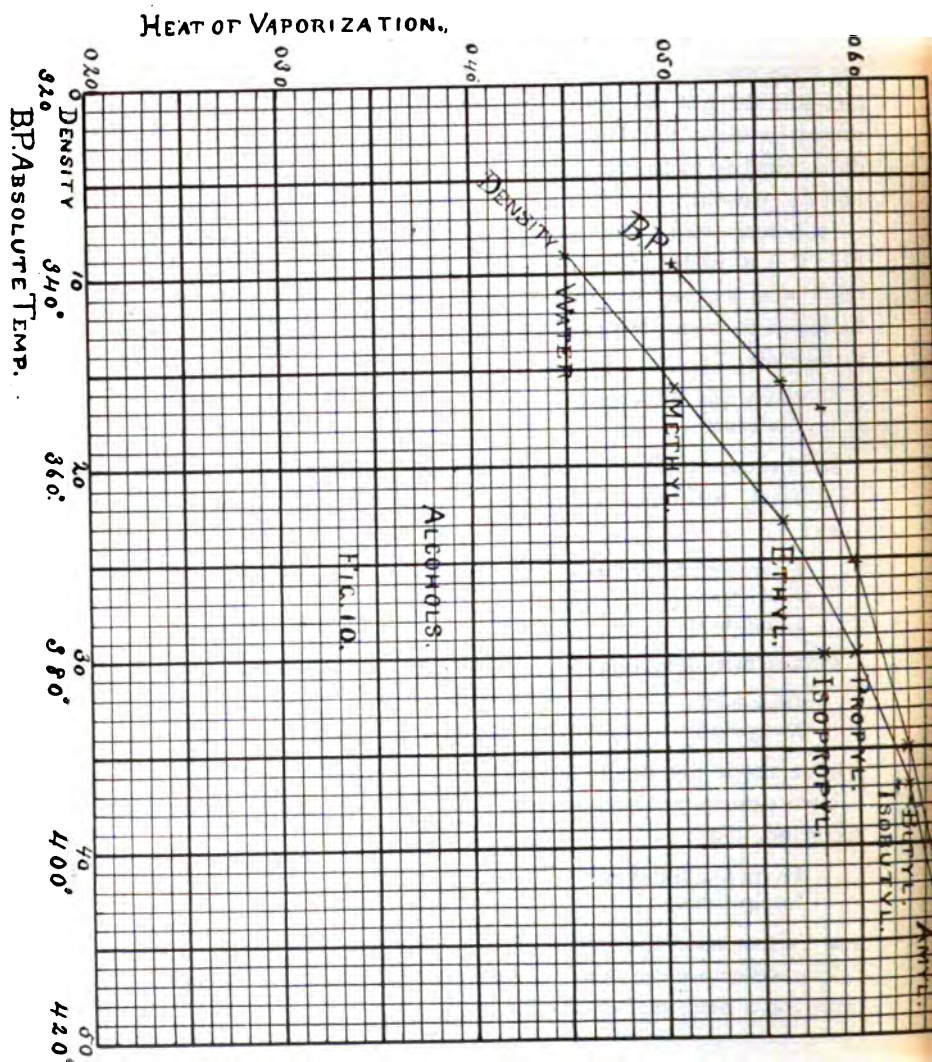


FIG. 10.

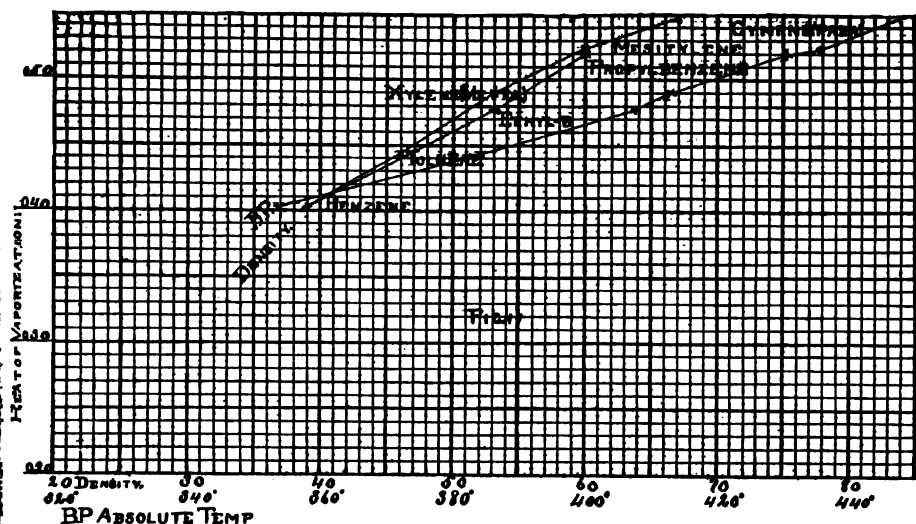


FIG. 11.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Benzene	$C_6H_6$	39	353.35°	0.8111	93.45 <sup>4</sup>	232.11	0.4026
Toluene	$C_7H_8$	46	383.8°	0.77694	83.55 <sup>4</sup>	188.49	0.4432
Ethyl benzene	$C_8H_{10}$	53	407.7°	0.7612	76.4 <sup>4</sup>	160.29	0.4766
Xylene (meta)	$C_8H_{10}$	53	412.9°	0.75715	78.25 <sup>4</sup>	159.44	0.4908
Propyl benzene	$C_9H_{12}$	60	430.2°	0.7399	71.75 <sup>4</sup>	137.63	0.5213
Mesitylene	$C_9H_{12}$	60	435.7°	0.7372	71.75 <sup>4</sup>	137.12	0.5232
Cymene	$C_{10}H_{14}$	67	448.0°	0.7248	66.3 <sup>4</sup>	120.73	0.5491

As will be seen in Fig. 11 these hydrocarbons form two density curves; one is formed by benzene, ethyl benzene, and propyl benzene, and the other by benzene, toluene, xylene, mesitylene, and cymene. The boiling-point curve is fairly regular and contains all of the series.

## CONCLUSION.

From the foregoing we may enunciate the following law, *viz.*:  
 "In any homologous series, the heat of vaporization in a unit of volume of the vapor, under the same conditions as to temperature and pressure, is proportional to the density and also to the absolute boiling-point."

It will be noticed that the acid radical in any series fixes the

<sup>4</sup> Schiff: *Ann. chem.* (Liebig), 234, 338.

characteristic of the curve, *i. e.*, the acid radical is the basis of the structure of the molecule, and the bases in combination with it, do not alter the general molecular architecture.

When more complete data have been obtained some interesting developments in this direction may be expected.

VANDERBILT UNIVERSITY.

## THE DETERMINATION OF METHANE AND HYDROGEN BY EXPLOSION.<sup>1</sup>

BY AUGUSTUS H. GILL AND SAMUEL P. HUNT.<sup>2</sup>

Received September 26, 1895.

IN making an analysis of illuminating gas by Hempel's method it was noticed that the determination of the constituents by explosion was by no means as accurate as that made by absorption. This had been observed by Hinman<sup>3</sup> and is probably due (1) to the fact that an aliquot part of the residue (after all absorptions had been made) containing the methane and hydrogen is used, necessitating the multiplication of errors by a factor as large as four or five, and (2) to the possible absorption of the carbon dioxide formed by the water in the burette. To obviate these difficulties, it was determined to use all the gas left after the absorptions had been made, mercury as the confining liquid and to explode with pure oxygen rather than with air. Instead of using the gas left after the actual absorptions, which would be of unknown composition and troublesome to obtain, an artificial mixture, made from methane, hydrogen and nitrogen, approximating closely to the composition of the residue, was employed.

*Preparation of the Gaseous Mixtures.*—The hydrogen was prepared by the electrolysis of water; it was then shaken up with potassium pyrogallate to remove the slight quantity of oxygen with which it was mixed, and upon analysis was found to contain four and two tenths per cent. of nitrogen. In making an analysis of hydrogen, we would lay especial emphasis upon the necessity of having the ratio of explosive mixture to inert gases as great as 1:6 as Hempel<sup>4</sup> recommends, in order not to burn the nitrogen.

<sup>1</sup> Prepared for the Springfield Meeting, August 28, 1895.

<sup>2</sup> The work described in this paper formed the basis of a thesis presented by Mr. Hunt to the Faculty of the Massachusetts Institute of Technology for the Degree of Bachelor of Science.

<sup>3</sup> Massachusetts Senate Document No. 16, 1892. Inspection of Gas and Gas Meters, p. 12.

<sup>4</sup> Hempel, "Gasanalytische Methoden" p. 132.



This is considerably larger than that which Bunsen<sup>1</sup> recommended, which may vary between the limits twenty-six and sixty-four of combustible gas to 100 of incombustible. Unless the larger ratio be adopted the determination of hydrogen may come two and a half per cent. high, as is shown by the following table:

TABLE I. DETERMINATION OF THE PURITY OF THE HYDROGEN.

Hydrogen taken cc.	Air used cc.	Ratio.	Per cent. hydrogen.
20.5	185.0	1 : 5.7	95.8
20.5	185.0	1 : 5.7	95.8
50.0	115.0	1 : 1.2	98.3
50.0	115.0	1 : 1.2	98.0

The nitrogen probably burns to  $N_2O$ , as the characteristic dark red fumes of this gas were frequently seen in the pipette. By the Griess test with  $\alpha$ -naphthylamine we were able to prove the presence of quite a quantity of nitrites in several cases.

In making the analyses of hydrogen by the first method it was necessary to connect and disconnect the burette three times in each case; the error which might be introduced was determined with the following results:

TABLE II. SHOWING THE ERRORS IN MANIPULATION IN CONNECTING THE BURETTE AND PIPE.

Burettefuls.	Air put in cc.	Air taken out cc.	Errors cc.	Remarks.
3	210.3	207.4	-2.9	No connections wired.
3	216.0	216.6	+0.6	
3	210.2	208.7	-1.5	
3	213.3	213.8	+0.5	All connections wired but one.
1	97.6	97.2	-0.4	
1	97.2	96.8	-0.4	All connections wired.
3	237.5	237.3	-0.2	

The oxygen was obtained in a similar manner to the hydrogen and contained one and six-tenths per cent. hydrogen and one and four-tenths per cent. nitrogen. The nitrogen in both these gases probably came from the distilled water electrolyzed, which was not freshly boiled before use.

The nitrogen employed was prepared by removing the oxygen from the air by means of phosphorus, allowing the gas to stand in the light twenty-four hours to decompose any ozone, and subsequent treatment with a small quantity of alkaline pyrogallate.

<sup>1</sup> Bunsen, "Gasometrische Methoden" (1877) p. 73.

An attempt was made to prepare the methane by the usual method of heating sodium acetate with sodium hydroxide and quicklime; the gas was found to be so largely contaminated with hydrogen,—as high as ten per cent. being found—as to be unfit for our purpose. This result is directly at variance with the statement of Freyer and Meyer<sup>1</sup> who say that this process “furnishes a very approximately pure gas.”

Nor did the method of Gladstone and Tribe,<sup>2</sup> the reaction of a zinc-copper couple upon methyl iodide, at first yield any better results, owing possibly to the water in the alcohol used. To obviate this and also prevent the possible formation of ethane, anhydrous methyl alcohol was substituted for the ordinary alcohol usually employed. The air in the apparatus was displaced by carbon dioxide and the methane collected, treated with potassium hydroxide to absorb this impurity. An analysis of the gas thus made, by explosion with oxygen and also with air—care being taken to avoid burning any nitrogen—showed the methane to be chemically pure.

The gases thus prepared and also the mixtures made from them, were stored in bottles provided with doubly-perforated rubber stoppers carrying a tube for the introduction of water and a tube for the egress of the gas. To render these absolutely tight, the stoppers were fastened in by fitting a brass plate to cover the top of the stopper, and by means of brass bolts and nuts passing through wire loops around the neck of the bottle, pressing the stopper firmly into the neck of the bottle. Joints of this kind are sufficiently tight to withstand a pressure of hydrogen.<sup>3</sup> To reduce the possibility of the transfusion of the gases to a minimum, a slight outward pressure was maintained in each bottle and it was inverted in a pan of water. The separate gases were kept in this way for about two months, freshly distilled water being used to displace the quantities requisite for the various mixtures. These mixtures made from them stood in no case over two days, before being completely used up, so that the amounts of methane and hydrogen dissolved by the distilled water, used to displace the various volumes taken, were negli-

<sup>1</sup> *Ztschr. phys. Chem.*, 11, 28.

<sup>2</sup> *J. Chem. Soc.*, 45, 154.

<sup>3</sup> Gill: *J. Anal. Appl. Chem.*, 6, 601.

ble ; the coefficients of absorption of the various gases not being widely different the ratio of the gases would remain the same within the errors of the analysis.

The gases were mixed by displacing the water from a liter bottle with the proper amounts of methane, hydrogen and nitrogen—measured by a burette—care being taken to leave some of the water to act as a stirrer, and then thoroughly shaking the bottle. By connecting this with a bottle of distilled water by means of a siphon, the requisite quantity of gas for an experiment could be displaced into the burette.

*Method of Procedure.*—Fifty cubic centimeters—this being about the usual residue from Boston gas after all the absorbable constituents had been removed—were measured out, mixed with about sixty cc. of oxygen and burned in an explosion pipette devised by one of us.<sup>1</sup> This combustion took place in different ways, at first as one explosion, and later by two explosions, with the idea of diminishing the error due to the possible combustion of nitrogen. In using the latter method it was found necessary to make the ratio of the explosive mixture to inert gases, nearly 1 : 2 in order that any explosion might take place ; with some mixtures not strong enough to explode, if care be not taken to pass the spark but a short time, the fine platinum wire becomes heated and finally glows, similar to the platinum sponge in the Döbereiner lamp, producing a very slow combustion, causing annoyance and delay in the analysis. A rough experiment may very well be made at first, to determine the composition of the gas under investigation and then suitable quantities of oxygen added for the first and second explosion.

The residue in the explosion pipette was, in every case, transferred to an ordinary Hempel burette for measurement, mercury, instead of water, being the confining liquid ; the gas was passed into potassium hydroxide and then into pyrogallate for the determination of carbon dioxide and oxygen. It is almost impossible to avoid sucking back some of the absorbents into the burette, which being strongly alkaline, would vitiate the next analysis by absorbing carbon dioxide ; to obviate this difficulty the instrument was washed out with dilute acetic acid<sup>2</sup> and then with

<sup>1</sup> Gill : *J. Am. Chem. Soc.*, 17, 771.

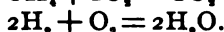
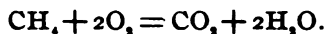
<sup>2</sup> If hydrochloric acid be used it forms a precipitate of mercurous chloride upon the walls of the pipette, coming from the mercurous salts produced by the action of the oxides of nitrogen upon the mercury.

water, almost filled with mercury allowed to stand about half an hour, the water which collected at the top displaced and then used for the next determination.

Instead of using the ordinary doubly bent connecting tube, this was varied by the introduction of a T joint, which is found especially convenient in adding successive portions of oxygen. The burette being connected at b, the pipette at p, and the oxygen at o, one can add the oxygen without disconnecting the burette each time. By connecting in a short tube at o, and filling it with mercury, the capillaries can be filled with mercury, an important point in preventing the rubber connectors from being burst by the force of the explosion. All connections should be carefully wired. By the use of two sets of apparatus two analyses may be executed at one time, in one an absorption be taking place, in another an explosion, etc. Six analyses in three hours were frequently made.



*Calculation of Results.*—The calculation of the results of the explosion was made according to the directions of Hempel,<sup>1</sup> that is in accordance with the reactions :



The volume of carbon dioxide obtained represents the methane present, and twice this volume subtracted from the total contraction, gives the contraction due to hydrogen; this latter being multiplied by two-thirds, gives the amount of hydrogen present. Table III shows the results obtained.

TABLE III.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY ONE EXPLOSION WITH OXYGEN.

Mixture cc.	Oxygen per cent.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
49.8	65.2	34.7	54.8	10.5
51.9	65.0	35.3	54.1	10.6
49.7	65.6	35.1	53.9	11.0
50.1	61.3	34.5	55.0	10.5
51.5	61.8	35.0	53.6	11.4
59.4	72.8	34.4	55.0	10.6
49.4	56.2	34.3	55.0	10.7
49.2	56.0	34.0	54.9	11.1
49.2	58.3	33.4	55.0	11.6
49.9	55.6	34.8	54.9	10.3
	Average	34.5	54.7	10.8
	Theory	34.7	53.5	11.8

*Loc. cit.* 217.

<sup>1</sup> *Loc. cit.*, 217.

The results obtained in the estimation of the methane are quite satisfactory and are probably within the limits of error of the apparatus. The hydrogen is high, due to the fact that the methane is low, and possibly also to the burning of the nitrogen.

In order to diminish the error from the latter source, a new mixture was made, and analyzed by exploding twice successively with oxygen, care being taken to add as little oxygen for the first explosion as would make the mixture combustible. Table IV shows the results obtained.

TABLE IV.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY TWO EXPLOSIONS WITH OXYGEN.

Mixture cc.	Oxygen used		Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
	first time.	second time.			
51.2	40.0	40.9	32.6	46.6	20.8
51.1	41.0	39.9	32.0	46.5	21.5
56.7	40.0	50.3	32.1	46.7	21.2
48.5	31.0	45.7	32.2	47.5	20.3
50.3	31.0	49.8	32.4	48.0	19.6
50.9	32.0	51.1	32.3	47.6	20.1
53.4	35.0	45.6	31.7	48.1	20.2
50.9	30.0	52.9	32.1	48.1	19.8
49.3	29.0	47.7	32.2	47.9	19.9
50.7	31.0	49.6	32.3	48.5	19.2
Average			32.2	47.55	20.25
Theory			32.2	47.7	20.1

The results are very satisfactory and if we compare them with those of the preceding table (III), we see that the average is more nearly correct than that of the former, and the deviations from the mean much less. The first three present the greatest variation in regard to hydrogen, it being one per cent. too low, these two had the greatest proportional amount of oxygen in the first explosion which is anomalous.

In order to obtain an idea of what takes place during the first explosion, several were performed and the per cents. of methane and hydrogen which burned determined.

TABLE V.—SHOWING THE AMOUNT OF METHANE AND HYDROGEN BURNED WHEN AN INSUFFICIENT QUANTITY OF OXYGEN IS PRESENT.

mixture cc.	oxygen cc.	Methane			Hydrogen		
		present cc.	burned cc.	burned per cent.	present cc.	burned cc.	burned per cent.
53.0	29.2	17.1	4.0	23.4	25.0	12.5	50.0
53.4	29.1	17.2	4.3	25.0	25.2	11.7	46.3
55.0	33.6	17.7	4.9	27.7	26.0	16.7	64.3
57.4	35.2	18.5	5.2	28.1	27.1	17.0	63.8

About sixty per cent. of the hydrogen burned and, contrary to the usual opinion, twenty-five per cent. of the methane and only about fifty per cent. of the oxygen.

By way of comparison with the usual method, a series of analyses of the same mixture was carried through, employing a smaller quantity and exploding with air; the mercury explosion pipette was used as before and the residue after explosion measured in a burette using water, as is customary, instead of mercury as the confining liquid.

TABLE VI.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY EXPLODING WITH AIR.

Mixture cc.	Air cc.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
17.8	79.8	29.8	45.3	24.9
15.3	82.2	31.4	49.3	19.3
16.3	81.4	33.7	42.5	23.9
15.9	82.4	31.4	38.6	30.0
16.1	78.2	39.1	30.4	30.5
16.8	80.5	33.3	42.3	24.4
16.1	82.0	30.4	44.1	25.5
16.2	81.2	36.4	33.4	30.2
15.8 <sup>1</sup>	79.5	31.6	40.0	28.4
15.1	82.5	33.8	38.0	28.2
16.2	82.6	31.2	42.9	25.9
14.8	83.8	34.4	38.4	27.2
15.9	84.3	33.9	37.7	28.6
	Average	33.1	42.2	26.7
	Theory	32.2	47.7	20.1
	Deviation	+0.9	-7.5	+6.6

These figures substantiate those of Hinman,<sup>2</sup> the results for methane and nitrogen being high and those for hydrogen low, the variations between the different analyses are even more marked. It is to be noticed that, contrary to expectation, the results upon the methane are high, indicating perhaps that the water in the burette is without appreciable solvent action upon the carbon dioxide formed. The discrepancy in the estimation of hydrogen is explained by the increase in the percentage of methane, any increment here being first doubled and subtracted from the "total contraction," and then approximately doubled in making the calculation, lowering as a consequence the hydro-

<sup>1</sup> These last five were measured after explosion with the mercury burette.

<sup>2</sup> *Loc. cit.*

gen by about four per cent., leaving three and five-tenths per cent. to be accounted for.

Almost the only supposition to account for this phenomenon is the somewhat anomalous one, that under these conditions the hydrogen is not completely burned.

In order to determine the effect of certain errors, such as the reading of the burette—graduated in fifths of a cubic centimeter—and any mistakes made in transferring the gases, the following assumptions were made (Table VII), and the deviations these might produce were calculated by the method of least squares, with the results showed in Table VIII.

TABLE VII.—SHOWING THE VOLUME OF GASES TAKEN AND THE ERRORS ASSUMED IN THEIR MEASUREMENT AND MANIPULATION.

	Oxygen method. cc.	error.	Air method. cc.	error.
Gaseous mixture taken.....	50.	0.15	15.	0.15
Oxygen (or air) used .....	60.	0.15	85.	0.15
Residue after explosion.....	33.	0.25	21.	0.25
Carbon dioxide formed.....	16.	0.25	5.	0.25

TABLE VIII.—SHOWING THE DEVIATIONS TO BE EXPECTED IN THE DETERMINATIONS OF THE VARIOUS GASES UPON THE ASSUMPTIONS IN TABLE VII.

	Oxygen method. per cent.	Air method. per cent.
Methane.....	0.51	1.64
Hydrogen .....	0.82	2.40
Nitrogen (by difference) .....	1.70	4.30

The results of this investigation may be summarized as follows:

- (1) The method of preparation of methane by heating sodium acetate, hydroxide and lime together does not yield a pure gas.
- (2) The method of determination of methane and hydrogen by one explosion yields results accurate to less than five-tenths per cent. of the methane and three-tenths per cent. of the hydrogen.
- (3) The method by two explosions yields results with in two-tenths per cent. of methane and three-tenths per cent. of the hydrogen.
- (4) When a mixture of hydrogen and methane is exploded with a quantity of oxygen insufficient for both, but more than sufficient for either, about sixty per cent. of the hydrogen and

twenty-five per cent. of the methane and fifty per cent. of the oxygen are consumed.

(5) The method of determination of the gases by one explosion with air gives results not within nine-tenths per cent. of the methane and seven and five-tenths per cent. of the hydrogen.

In concluding this article we would express our indebtedness to Mr. R. B. Price for preliminary work which served as the foundation of this thesis.

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### NEW BOOKS.

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. BY E. P. HARRIS, PH.D., LL.D., Professor of Chemistry in Amherst College. New edition. Thoroughly revised and corrected. Amherst, Mass.: Carpenter & Morehouse. 1895. pp. 308. Price \$1.50.

The author of this book is a veteran teacher, and this new edition is the result of the experience of his laboratory teaching for over a third of a century. The book is divided as follows:

Part I. Examination of solutions: Sec. I, Bases; Sec. II, Acids.

Part II. Examinations of solids.

Part III. Qualitative separations: Sec. I, Bases; Sec. II, Acids.

Supplement: Reaction of rare elements; Use of the spectro-scope in analysis.

Appendix: Preparation of reagents; Table of solubility; Index.

Part first gives the reactions of each of the metals and acids, and is interleaved that the student may write out the reaction-equations on the blank pages. This is intended to be used in connection with unknown solutions containing a single base and acid.

Part second is a guide to the systematic examination of solids according to the plan which was first introduced by the author and has since been very generally adopted. This is perhaps the most valuable part of the book.

Part third takes up the separations of metals systematically, using the methods which have proved most satisfactory in the Amherst laboratory. Alternate methods are in a number of instances given, but generally only a single method; the idea is to avoid confusing the student with a number of different ways of working, the relative merits of which he is incapable of estimating. This part is very complete, covering practically all cases



with the common metals and acids, while it is well supplemented by a very comprehensive chapter on the reactions of the rare metals.

The appendix on the preparation of reagents will be found useful to teachers.

This manual is not intended to merely make the student a good analyst ; it is rather a manual of instruction in chemistry through the medium of qualitative analysis. It is not a book for self-instruction, but it is intended that the student shall have the constant supervision of an instructor. As a manual for college students it does not appear to be too much to say that of all the many books of its class it is the best.

JAS. LEWIS HOWE.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY. VOL. II. FERTILIZERS. Cloth, 8 vo. pp. 332. Easton : Chemical Publishing Co. 1895. Price, \$2.00.

The official inspection of fertilizers involves such great pecuniary interests that the chemical methods used for the purpose are matters of the highest importance to analyst and manufacturer. All countries in which fertilizers are used to any extent have some plan of inspection and certain methods of conducting the chemical work required. These methods are the result of very numerous and often difficult investigations of the men best qualified to deal with the subject.

In the volume under consideration the subject of fertilizers is treated under four heads : (1) Phosphates and phosphatic fertilizers ; (2) Nitrogen in fertilizers and fertilizing materials ; (3) Potash in fertilizing material and fertilizers ; (4) Miscellaneous fertilizers, lime, gypsum, ashes, coarse manures, etc.

The matter of drawing samples of various materials receives a deservedly large share of attention. Then the analytical work proper is taken up and treated very fully and clearly. The different analytical methods of various countries are given in full and a brief but very valuable discussion of the merits of the methods follows. In many cases the value of the discussion is increased by full statements of analyses.

The matter thus brought together consists of both original matter and material published at home and abroad ; and often published in such a way as to be now inaccessible to many workers on the subject.

The treatment of the subject is full, clear, systematic, and well up to date. Enough technology is included to show the reader the reason for the methods used in the work ; and the author has not lost sight of the fact that he is writing on the principles as well as the practice of agricultural analysis.

The chemist who has been unfortunate enough to buy a number of alleged treatises on agricultural chemical analysis (chiefly of English origin) that have recently appeared will fully appreciate the merits of this work and heartily thank Dr. Wiley for producing a work that is full and reliable. For if the investigator of questions bearing on the analysis of fertilizing material does not find here methods suitable for the purpose he has in view, he may as well resign himself to working the matter out for himself.

To the teacher the book is of very great value, and if used by students they will have the satisfaction of knowing that they are well prepared for technical work in factory or inspection laboratories.

The full citation of authorities and an unusually complete table of contents and index are commendable features of the work.

In the preface, the author regrets "that the contents of the volume have again exceeded all expectations." His readers will not share this regret, for there is nothing here that could have been omitted to advantage.

It is to be hoped that there may be no delay in the appearance of the remaining volumes of a work that is of such high value to those who wish to keep informed on so wide a range of chemical work as is included under the term agricultural analysis.

H. A. HUSTON.

LABORATORY WORK IN CHEMISTRY. A SERIES OF EXPERIMENTS IN GENERAL INORGANIC CHEMISTRY. BY EDWARD H. KEISER. 8 vo. viii, 119 pp. New York : American Book Co.

This little book, in spite of its name, is not exclusively a laboratory guide nor is it exclusively devoted to experiments in inorganic chemistry. Thus, we find (p. 62) a definition of *equivalent*, and a description of the properties of carbon (p. 94). The experiments relating to the organic compounds, marsh gas,

ethylene, and calcium carbide do not strike one as being very instructive or *apropos* of anything in particular.

An excellent feature is the introduction of numerous questions, although these might, perhaps with advantage, have been more closely confined to the subjects of the experiments. It is not easy to see, for example, why such a question as the following should be brought into a laboratory manual: "Which elements make up three-fourths of the solid crust of the earth?"

A number of the more difficult experiments, such as the gravimetric determination of the composition of water are to be performed by a few more advanced students for the benefit of all, a commendable arrangement when the classes are not too large.

The experiments are, in the main, well selected and described in simple and clear English. The use of the term "arseniu-retted hydrogen" is a curious anachronism in a book which for the rest adheres to a modern nomenclature.

L. W. ANDREWS.

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#### BOOKS RECEIVED.

Kentucky Agricultural Experiment Station, Bulletin No. 56. Analysis of Commercial Fertilizers. Lexington, Ky.

Kentucky Agricultural Experiment Station, Bulletin No. 57. (1) Wheat Experiments. (2) Oat Experiments. Lexington, Ky.

Texas Agricultural Experiment Station, Bulletin No. 36. Vegetable Insecticides. College Station, Brazos County, Texas.

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#### NOTE.

*The Banquet to Messrs. Mond and Tyrer.*—Two prominent English chemical manufacturers, Messrs. Ludwig Mond, a member of the well-known firm of Brunner, Mond & Co., and Thomas Tyrer, a manufacturer of pharmaceutical chemicals and now President of the Society of Chemical Industry, have been paying a visit to the United States. There has naturally been considerable desire among American chemists to meet these gentlemen, and they have received many invitations and courtesies. An account of Mr. Tyrer's visit to the meeting of the

Lehigh Valley Section of the American Chemical Society will be found in the Proceedings issued with the November number of this Journal.

On the evening of November 1, ninety-one chemists took part in a farewell banquet at Delmonicos. The after-dinner speakers were Mr. Alfred Mason, of New York, who presided, Thomas Tyrer, Ludwig Mond, Peter Townsend Austen, Seth Low, W. H. Nichols, and H. W. Wiley. Impromptu remarks were also made by J. H. Appleton and Walter H. Bunn. A verbatim account of the remarks made is contained in the *New York Oil, Paint and Drug Reporter*, November 4, from which this account is condensed.

It is quite impossible in the space available to do justice to all that was said. The addresses made were all enjoyable, some of them brilliant, and the festivities were ably and wittily directed by Mr. Mason.

Mr. Tyrer, who spoke for the Society of Chemical Industry, after referring to the early history of the Society, expressed his appreciation of the courtesies received during his visit, his belief in the greatness of our industrial future, and his admiration of our institutions of learning.

Professor Austin spoke for the N. Y. Section of the American Chemical Society. Among other things, he said:

"In this country the practical chemist and the teacher have little time left for purely scientific research and in this we cannot compete at present with Europe. But I am sure the time will come when we can. I have unlimited confidence in American brains. Industrial chemical investigation is no less difficult, no less honorable than purely scientific research. If any investigator in pure science doubts this let him try his hand at cracking some technical nut. Let him, for instance, get up a profitable process for making sodium permanganate for our colleague, Mr. Tyrer. \* \* \* What we need now in this country is the establishment of departments of chemical engineering in our larger colleges. \* \* \* To understand the chemistry of manufacturing is one thing, to be able to handle a chemical reaction mechanically is quite another matter."

Mr. Mond responded for the guests, he said:

"I feel proud that while so many miles from home I am yet no stranger among you. \* \* \* Professor Austen has remarked that investigation in technical chemistry is quite as difficult as investigation in pure science. There is, however, this great difference that investigation in

pure science bears fruit for centuries to come. Every discovery of new truth is an increase of knowledge and is a benefit to humanity. Technical matters come and go and make room for more perfect methods as time goes on. It is therefore true that a man who devotes himself to pure science deserves the gratitude of future generations as well as his own. We live more for our children and grandchildren than for ourselves, so we cannot do too much in encouraging men who are ready to devote their lives to the betterment of the future. It is extremely natural that in an immense country like this—but it is not right to call it a country or a continent; it is a hemisphere; it is half of this globe—that the few who develop this branch of science shall have little time to think of posterity. In looking at the magnificent institutions that have grown up in this country for the study of science I have very little doubt that the time is not far distant when very many of you will appreciate the importance of pure science more than you have ever done before, and the time will not be far distant when the number will be large enough to meet the wishes of men of science among you."

Mr. W. H. Nichols responded for the Chemical Manufacturers. He said:

"That knowledge is power is true, but how can it be power without the application of it, and how can we have the application without the engineer. \* \* \* There is one other thing in which we can imitate our friends on the other side of the water to advantage, and that is the way in which they come together and compare notes, and receive from one another benefits from the experience each has attained. In this country we have not grown enough to know not to be afraid of each other, and the manufacturing chemist of the United States is hiding his head in the sand like the ostrich \* \* \* \* \* In the census of 1890 it was ascertained that there were 1626 manufacturing establishments in the United States. They employed a capital of over one hundred and sixty-eight million dollars, and hired property of the value of twelve million dollars, employing in the aggregate nearly 44,000 persons, and paying a total wage of more than twenty-five million dollars. I desire to call the attention of our guests to one or two facts connected with these employes. Of the total number a little less than 4,000 were females, but only 346 were children. That is one of the best statements I can make to show the condition of the manufacturing industry that it has been necessary to employ only 346 children."

The arrangements for the banquet were in the hands of a committee with J. H. Wainwright as chairman. They were well planned and the occasion was a most enjoyable and profitable one.

E. H.

*Errata.*—Page 759, October Number, in the table headed " $\text{MoO}_3$  in sample 10 Phosphomolybdate" the line Doolittle (Job) 90.47, 93.05, 95.80, should read Doolittle (Job) 89.88, 92.45, 95.18.

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### A TRIBUTE TO PASTEUR.<sup>1</sup>

A FEW weeks ago, one of the foremost scientists of the present century passed into the great beyond. Louis Pasteur, although a master mind in physics and geology, was preeminently a chemist, therefore it behooves our Society to express its regrets at the great loss sustained not only by France, but which the whole civilized world is obliged to bear. Men like Pasteur, whose life was spent in disseminating broad principles of truth, in alleviating pain, in mitigating epidemic diseases and in exterminating parasites whose activity threatened ruin to the agriculturists, cannot be narrowed down as belonging to one country; but on the contrary are veritable cosmopolites, deservedly honored and venerated by every nation.

It is not my intention to give a sketch of the life of Pasteur, but simply to call your attention, in a brief way, to some of his most important contributions to science and the effects produced. The one, that undoubtedly tended towards moulding his thoughts in the direction to which he devoted his best years was to combat the idea of Heterogenesis and it may truthfully be said that he succeeded in making it untenable by incontestable evidence in support of his theory, that: "The living organized ferments spring only from similar organisms likewise endowed with life; and that the germs of these ferments exist in a state of suspension in the air or on the exterior surface of objects." This not only disproved Fremy's Hemi-organism hypothesis but also Liebig's assertion that "The cause of fermentation is the internal molecular motion, which, in the course of decomposition, is communicated to other matter in which the elements are connected by very feeble affinity." Pasteur, by means of most thorough and extensive research, from 1857-61, simply forced the attention of everybody to the physiological side of the subject, and by absolutely unimpeachable evidence, proved that Schwann's views are correct. Of the investigation, both synthetical and analytical, it is impossible to speak otherwise than in terms of the highest admiration. Even the purely critical portion of Pasteur's work would be enough to immortalize his name. His theory, "That the chemical act of fermentation is

<sup>1</sup>Read before the Cincinnati Section, Oct. 15th.

a correlative phenomenon of a vital act, beginning and ending with it," notwithstanding the thousands of experiments since made by him and other investigators remains unshaken and is to-day the firm basis of all ideas respecting fermentation. Pasteur's researches, by their precision, the care taken to avoid all sources of error, and his rigorous exactness, removed every suspicion of the intervention of germs brought from without or pre-existing in the liquid operated on, a difficulty on which all discussions between heterogenists and panspermists had heretofore turned. By means of the organic corpuscles of dust mixed with amorphous ones, obtained by filtering air through a gun-cotton plug and showing that their absence prevented sterilized fluids from fermenting, but their presence would cause it to set in, Pasteur elevated a hitherto merely observed phenomenon to a scientific basis. His experiments with the forty flasks of must, to show that the ferments which cause the fermentation in the vintage tube, must come from the exterior and not the interior of the fruit, as well as those made to discover quantitatively the germs in the air, are famous.

Pasteur's signal success in counteracting the effects of Pebrine which threatened to destroy the silk industry of France and Italy, not only saved thousands from absolute ruin but taught the people that infectious diseases could be combated by a most novel method. Consequently his efforts toward suppressing the ravages produced by chicken cholera and splenic fever met with less popular prejudice. While experimenting on chicken cholera he produced cultures of varying degrees of virulence by permitting sufficiently long intervals to elapse between the impregnation of one culture with the microbe of the preceding. Furthermore, he proved that each culture of attenuated virulence reproduced the virulence of that which had served as the starting point; concluding from these experiments that the oxygen of the air was the possible cause of the attenuation. When fowls had been rendered sufficiently ill by the attenuated virus which the vital resistance arrested in its development, immunity from the original disease arose. Perhaps one of the most brilliant triumphs achieved by Pasteur consisted in taking advantage of the morphological changes taking place in the Anthracoid

microbe. He prevented it from producing corpuscle germs, kept it while in this condition in contact with oxygen, days, weeks, and months, and thus produced a series of attenuated virulences. With this vaccine he practically exterminated the splenic or carbuncular disease throughout France.

To Pasteur we owe nearly all of our knowledge of the relations between the optical activity and crystalline form in tartaric acid. He showed that enantimorphism depended upon hemihedral forms of the rhombic system. His experiments in this direction led to the discovery of physiological asymmetry and paved the way for the study of elective fermentation. He proved that substances chemically and physically the same save in their opposite rotatory power can serve in one case as nutrients to certain organisms and in the other are worthless as such; and that only certain geometrical forms can serve the requirements of the cells. Thus we see Pasteur as one of the pioneers in the field of stereochemistry.

His successful method of counteracting rabies, his untiring labors in the interest of suffering humanity up to the time of his death forcibly recalls Tyndall's letter, written as far back as 1876. "For the first time in the history of science, we are justified in cherishing confidently the hope that, as far as epidemic diseases are concerned, medicine will soon be delivered from empiricism and placed on a real scientific basis; when that great day shall come, humanity will, in my opinion, recognize the fact that the greater part of its gratitude will be due to you."

Believe me ever faithfully yours,

JOHN TYNDALL.

France can well be proud of such sons as Lavoisier and Pasteur. Generations to come will recognize in their labors the possibility of unveiling, by means of conscientious scientific research, nature's most carefully treasured secrets.

Indeed Longfellow must have had such men in mind when he wrote,

"Lives of great men all remind us  
We can make our lives sublime,  
And, departing leave behind us  
Footprints on the sands of time."

ALFRED SPRINGER.

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## Proceedings.

### NEW MEMBERS ELECTED NOV. 30, 1894.

Alexander, Heald H., care of Globe Smelting and Refining Company,  
Denver, Colo.

Donaldson, Sidney T., Frost Laboratory, 34 Broad St., Charleston, S.C.

Eddy, Harrison P., City Hall, Worcester, Mass.

Fuller, Fred. D., Durham, N. H.

Guiteman, Franklin, Cooper Block, Denver, Colo.

How, Fred W., Durham, N. H.

Leighton, Virgil L., A.B., Lawrence, Kan.

McKeen, James, Tilly Foster, Putnam Co., N. Y.

Morse, Prof. Fred W., Durham, N. H.

Parmly, Dalton, Sharpville, Pa.

Proctor, Richard W., care of Wm. S. Merrell Chemical Company,  
Cincinnati, Ohio.

Schaeffer, Henri, Manchester Mills, Manchester, N. H.

Sherman, H. C., College Park, Md.

Stone, Edward P., Durham, N. H.

Tonceda, Enrique, Hoosick Falls, N. Y.

Traphagen, Dr. F. W., Bozeman, Mont.

Ullman, Dr. H. M., Lehigh University, South Bethlehem, Pa.

Veitch, F. P., College Park, Md.

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### ELECTED DEC. 10, 1894.

Allen, W. M., Raleigh, N. C.

Clarke, Thomas, Chapel Hill, N. C.

Clymer, Edwin S., 1012 North 10th St., Reading, Pa.

Cooke, George T., 103 Milk St., Boston, Mass.

Field, Charles, 3rd, 2013 Green St., Philadelphia, Pa.

Glover, Henry, East Falls of Schuylkill, Philadelphia, Pa.

Harris, J. R., B.S., Johns Hopkins University, Baltimore, Md.

Irish, Cyrus W., Lowell High School, Lowell, Mass.

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Mason, A. H., F.C.S., F.R.M.S., care of Seabury and Johnson, 59 and 61 Maiden Lane, New York City.

Miles, George W., Jr., 103 Milk St., Boston, Mass.

Peter, Alfred M., 171 Rose St., Lexington, Ky.

Prentiss, George N., 226 Grand Avenue, Milwaukee, Wis.

Sanders, C. N., Pulaski City, Pulaski Co., Va.

Scovell, M. A., Lexington, Ky.

Seldner, Rudolph, 217 Jefferson Avenue, Brooklyn, N. Y.

Siegfried, Alfred A., 39 South St., Jersey City, N. J.

Smolt, Frank O., Aspen, Colo.

Waite, Charles N., Rumford Falls, Me.

#### CHANGES OF ADDRESS.

Brown, W. G., Division of Chemistry, Department of Agriculture, Washington, D. C.

Forbes, Fred B., Experiment Station, Lawrence, Mass.

Hewitt, Edward R., Room 8, East 9th St., New York City.

Mumper, W. N., 228 West State St., Trenton, N. J.

Waterman, C. N., 345 Decatur St., Brooklyn, N. Y.

Weems, J. B., Experiment Station, Geneva, N. Y.

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### MEETINGS OF THE SECTIONS.

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#### NEW YORK SECTION.

Friday Evening, Dec. 14, 1894.

Prof. P. T. Austen, presiding.

Forty members present.

Dr. Thomas B. Osborne, of New Haven, read a paper on the Chemical Nature of Diastase, showing that by successive treatment with ammonium sulphate, solution in water, dialysis into alcohol, and extraction with sodium chloride solution, a nitrogenous substance can be prepared from malt extract which has an enormous diastatic power, and that by this means pure diastase may be isolated.

Dr. Bartley presented facts to prove the injurious effects of

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glucose upon the digestion, and commented upon the probable reasons therefor.

Prof. Austen presented an essay upon careless diction in chemical text-books.

#### WASHINGTON SECTION.

Nov. 8, 1894.

President W. H. Seaman in the chair.

Ten members present.

The resignation of Prof. J. C. Gorden was read and accepted.

A letter from John W. Hoyt was read, asking the co-operation of the Society in the formation of a National Post-Graduate University. The President of the Society was asked to assure Mr. Hoyt of the sympathy and co-operation of the Society.

H. W. Wiley reported as to the First Congress of Chemists at the San Francisco Exposition, and referred to the probable formation of a Local Section of the American Chemical Society on the Pacific Coast.

A paper was read by W. D. Bigelow on the "Coloring Matter in California Red Wines." This was a preliminary notice of work, not yet completed, which will later be made the subject of a more extended communication. He had subjected samples of ninety-four varieties of California red wines to the same examination as that commonly applied for the coloring matter in European wines. "According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. Sometimes, however, a gray, or yellowish, or orange-gray precipitate or solution is obtained with reagents which are said to give a green or grayish-green with French wines. On the other hand, no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments."

#### *Discussion.*

Dr. Wiley said that the inducements for adulteration of California wines were not great on account of their low price. The difficulties in distinguishing between a natural and a spurious

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article became very great at a point where the results of analyses might just as readily be interpreted one way as another, and to obtain greater certainty beyond this point the work was undertaken in the laboratory of the Agricultural Department.

Mr. Bigelow, in response to the question as to the success of the use of the spectroscope in the examination of wines, said that it had been employed with some success in the detection of cochineal and of the coal-tar colors, but for the detection of vegetable colors it was unsatisfactory, owing to the fact, no doubt, that they were so closely allied to the natural colors of the wine.



## Proceedings.

### ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The tenth general meeting of the American Chemical Society was held in Boston and Cambridge, Mass., Dec. 27th and 28th, 1894.

The Society was called to order at 10.20 A. M., Thursday, Dec. 27th, at the Massachusetts Institute of Technology, in room No. 22, of the Walker building.

Dr. T. M. Drown made a brief address of welcome to which President Wiley responded on behalf of the Society. Dr. Wiley expressed the special pleasure which the visiting chemists felt in meeting in the Massachusetts Institute of Technology, an Institution which has done so much for the advancement of science.

Mr. C. Tennant Lee, chairman of the Local Committee of Arrangements, made some announcements, and stated that on account of the inclement weather it would hardly be expedient to carry out the program which had been arranged for visits to the Experiment Station of the State Board of Health, and the Rubber Shoe Manufactory at Malden during the afternoon.

The minutes of the last general meeting were read and approved, and the minutes of the former meetings were also approved, as recorded by the General Secretary.

The General Secretary then read his annual report, which was as follows:

TO THE MEMBERS OF THE AMERICAN CHEMICAL SOCIETY:

GENTLEMEN: In presenting my annual report at the close of the present administration, a brief retrospective view of the organization and development of the Society, and a glance at its present condition will enable the members to gain instruction and encouragement from the past, hope and inspiration from the present, and a bright and confident outlook upon the future.

The American Chemical Society was the outgrowth of a

meeting of American chemists held in Northumberland, Pa., in August, 1874, to celebrate the centennial of the discovery of oxygen by Priestley. The Society was organized in 1876 and incorporated October 25, 1877. Its inception was vigorous, and those who took part in its organization had high hopes for the position it would occupy among the scientific societies of the world, for the inspiration and aid it would afford those who were engaged in chemical pursuits or in preparing others for such vocations, and for the ever increasing stimulus it would furnish to chemical science and industry throughout the American continent.

From the beginning the Society published regularly a Journal of its proceedings, including papers and discussions; many of the leading chemists of the country were enrolled in its membership; quite a number of prominent chemical manufacturers were among its associates; and the names of foreign chemists of distinction were upon its roll, either as active or as honorary members.

The following is a list of persons who have served the Society as its President:

*1876, J. W. Draper.	1886, A. B. Prescott.
*1877, J. Lawrence Smith.	1887, C. A. Goessmann.
1878, S. W. Johnson.	*1888, T. Sterry Hunt.
*1879, T. Sterry Hunt.	1889, C. F. Chandler.
*1880, F. A. Genth.	1890, H. B. Nason.
1881, C. F. Chandler.	1891, G. F. Barker.
1882, J. W. Mallet.	1892, G. C. Caldwell.
*1883, J. C. Booth.	1893, H. W. Wiley.
*1884, J. C. Booth.	1894, H. W. Wiley.
*1885, J. C. Booth.	

It is not until within the past few years, however, that the Society has fully justified the hopes of its founders that it would be in all respects a representative national organization. Its membership extended throughout the entire country and even included persons of other countries upon our own continent and in Europe, but, inasmuch as the meetings were all held in New York City, the members in other localities did not come into so active relation with the Society and its work as was desirable, and could not be prevailed upon to take sufficient interest in its

\* Deceased.

welfare, nor to assume their share of responsibility in its management. Under these conditions there gradually developed among the members in other parts of the country the erroneous impression that the Society was local rather than national in its efforts and aims, and this impression was deepened by the fact that a number of prominent chemists throughout the country had either never been members of the Society or had withdrawn from active connection with it.

This state of affairs was unsatisfactory to every one, and it devolved heavy burdens upon the members residing in New York City and vicinity. There was no alternative, however; those members were obliged to carry the burden with heroic self-sacrifice until some plan could be devised by which the interest and active co-operation of a large body of chemists throughout the country could be permanently enlisted. To this end they labored with persistent determination and with unshaken faith in the ultimate result. The American Chemical Society had been recognized abroad for years as the organized body of the chemists of North America; it had already acquired something of prestige and established rights; and those who were made responsible for its management believed that it could be made to command the active support of the chemists of this continent, and to secure for them and their work adequate recognition among the chemists of the world.

The conferences, struggles, concessions, appeals to American chemists everywhere, whether members of the Society or not, and the hearty response to those appeals which was received from all over the country, need not be recounted here; but they will ever remain a noble example of self-sacrifice and true devotion to the welfare and progress of chemical science upon this continent.

The plan finally adopted by the chemists who had part in these counsels and efforts was to utilize what the American Chemical Society had already gained, to broaden and strengthen its foundation, and to effect radical changes in its management and operations. These changes were so outlined and provided for by the Society as to induce large numbers of prominent chemists, who had hitherto held aloof, to become members of the

Society and to add their influence, their energies, and their counsel to the forces that were already in operation to secure a complete and satisfactory reorganization of the Society.

Among the most effective measures adopted and continued up to the present time are the following :

(1) The management of all the important affairs of the Society is entrusted to a council of fifteen, composed of twelve members regularly chosen by ballot at the annual election of the Society—four elected each year, to serve for a period of three years—and in addition, the President, the General Secretary, and the Editor, *ex-officio*. The members of the council for the year 1894 are :

H. W. Wiley, Washington, D. C., President.  
 Albert C. Hale, Brooklyn, N. Y., General Secretary.  
 Edward Hart, Easton, Pa., Editor.  
 J. H. Appleton, Providence, R. I.  
 G. F. Barker, Philadelphia, Pa.  
 G. C. Caldwell, Ithaca, N. Y.  
 F. W. Clarke, Washington, D. C.  
 C. B. Dudley, Altoona, Pa.  
 W. L. Dudley, Nashville, Tenn.  
 J. W. Mallet, Charlottesville, Va.  
 Wm. McMurtrie, New York, N. Y.  
 T. H. Norton, Cincinnati, O.  
 A. B. Prescott, Ann Arbor, Mich.  
 Alfred Springer, Cincinnati, O.

(2) Local sections are established in different parts of the country, after the plan of the British Society of Chemical Industry. The presiding officers of the sections constitute the vice-presidents of the Society. Six local sections exist now, and there is a good prospect for the early formation of two or three more. Those already chartered are :

Rhode Island Section : Presiding Officer, Charles A. Catlin, 133 Hope St., Providence, R. I. ; Secretary, E. E. Calder, Board of Trade Building, Providence, R. I.

Cincinnati Section : Presiding Officer, J. U. Lloyd, Court and Plum Sts., Cincinnati, O. ; Secretary, E. C. Wallace, Room 71, Blymeyer Building, Cincinnati, O.

New York Section : Presiding Officer, Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y. ; Secretary, Morris Loeb, 37 East Thirty-eighth St., N. Y. City.

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Washington Section : Presiding Officer, W. H. Seaman, 1424 Eleventh St., Washington, D. C. ; Secretary, A. C. Peale, 605 Twelfth St., Washington, D. C.

Lehigh Valley Section : Presiding Officer, W. H. Chandler, South Bethlehem, Pa. ; Secretary, Albert H. Welles, Lafayette College, Easton, Pa.

New Orleans Section : Presiding Officer, A. L. Metz, Tulane Medical College, New Orleans, La. ; Secretary, Hubert Edson, Bartels, La.

(3) Two general meetings of the Society are held each year, the time and place of these meetings being determined by the council. General meetings have been held as follows :

1. Newport, R. I., August 6 and 7, 1890.
2. Philadelphia, Pa., December 30 and 31, 1890.
3. Washington, D. C., August 17 and 18, 1891.
4. New York, N. Y., December 29 and 30, 1891.
5. Rochester, N. Y., August 16 and 17, 1892.
6. Pittsburg, Pa., December 28 and 29, 1892.
7. Chicago, Ill., August 21 and 22, 1893.
8. Baltimore, Md., December 27 and 28, 1893.
9. Brooklyn, N. Y., August 15 and 16, 1894.

The change in membership during the past few years, since it was decided to arrange for general meetings of the Society to be held semi-annually in different localities, may be seen from the following statistics taken from the list of members published each year :

Nov. 1889,	169	members,	28	associates,	8	honorary	members.
Nov. 1890,	203	"	27	"	8	"	"
Nov. 1891,	269	"	24	"	9	"	"
Nov. 1892,	319	"	25	"	7	"	"
Sept. 1893,	423	"	30	"	7	"	"
Sept. 1894,	664	"	50	"	8	"	"
Dec. 1, 1894,	700	"	55	"	8	"	"
" 26, 1894,	720	"	55	"	8	"	"
Total, 783.							

The present status as to membership should be given as follows :

Official roll of members.....	783
Elected but not required to qualify before Jan. 1,	
1895 .....	37
Applications now pending, no doubt of election...	30

Total..... 850

By inspection of the foregoing figures it will be seen that the membership of the Society has more than doubled during the past two years, and has more than quadrupled since November, 1889.

(4) The Journal of the Society appears on the first of each month throughout the year, each number containing at least seventy-two pages, making a yearly volume of the minimum size of 864 pages. It has been found necessary, however, to enlarge the size of some of the numbers, and that for December, 1894, includes about 100 pages of papers and discussions in addition to proceedings, etc. It is the intention of the Society to make this the leading and representative chemical journal of the United States, and one of the most important scientific periodicals to be found anywhere. It will contain the papers read before the various sections of the Society and before its general meetings, together with such abstracts relating to the progress of chemical science and industry as may be necessary. A prominent feature will be its effort to represent industrial and commercial chemistry. Each branch of chemical science will receive due attention and support, and those engaged in any kind of chemical research, or in the application of chemistry to the arts, will find in the JOURNAL a wide scope for publication. Through this medium the followers of each branch of chemistry will be brought into intimate contact with each other, and will know also what those in other branches of chemistry are doing, and what progress is making in all directions.

During the year 1894, by order of the council, the General Secretary has been charged with the duty of collecting all the membership dues. A large amount of arrears has been collected, and we believe that the percentage of arrears at present is lower than ever before. The financial report of the General Secretary is presented in a separate statement.

At the beginning of the year, Edward Hart was reappointed editor, and the regular standing committees for the year were selected.

A committee, consisting of F. W. Clarke, Chairman, Albert C. Hale, Secretary, and W. L. Dudley, was appointed by the President, on authority of the council, to receive and consider

suggestions for amending the constitution, the main object sought being to have only one governing body for the Society, instead of two—the Council and the Board of Directors—as at present; this body to be selected from the membership without regard to the locality of their residence.

By the action of the Board of Directors the General Secretary was instructed to place on file a certificate of incorporation of the Society, signed by all of the directors, and so worded that the majority of the Board of Directors shall not be required to be residents of the State of New York. Upon presenting such certificate at the office of the Secretary of State in Albany, N. Y., it was rejected on the ground that, under the laws now existing such an amendment can not be made. Upon this, the Board of Directors, with the recommendation of legal counsel, took the following action: "*Resolved*, That the Board of Directors hereby request the American Chemical Society, at its annual meeting, to authorize the taking of such steps as may be necessary to secure the passage of a bill by the Legislature of the State of New York, which shall so change the present laws of the State as to allow the Society to choose its directors without regard to their being residents of the State of New York, or of any other State or locality."

At the summer meeting of the Society, held in Brooklyn, N. Y., August 15 and 16, 1894, Dr. Wolcott Gibbs, of Newport, R. I., was unanimously elected an honorary member of the Society. This is the first time an American has been elected to honorary membership. Upon being informed by telegraph of this action, Dr. Gibbs sent a reply expressing his sincere thanks to the Society, and his high appreciation of the honor they had conferred upon him. An engrossed certificate of his election, signed by every member of the council, has been forwarded to Dr. Gibbs in accordance with the provisions of the constitution.

During the year, charters have been granted by the Board of Directors for the formation of two new local sections, on Feb. 15, for the Lehigh Valley Section, and August 15, for the New Orleans Section. The charters for both of these have been forwarded and the Sections have been organized.

The outlook has never before been so promising as it is to-day.

The Society is now founded upon a broad and strong basis, and its mode of organization allows a ready modification of its management whenever experience may indicate that changes are desirable. The plan of holding general meetings twice a year, in different localities, strengthens the Society, rapidly extends its influence, and brings the chemists of the country into personal acquaintance with one another and into a knowledge of the vast amount of successful work which is done by them upon this continent. The formation of local sections deepens the interest felt in the general Society, and stimulates scientific activity and enterprise in those localities where such sections are established. The growth of the Society in numbers and influence has been almost phenomenal within the past few years, and when we consider its present attainments, and the number and standing of those who are now upon its roll of membership we may confidently assert that the American Chemical Society to-day takes rank with the leading organizations of its kind in the civilized world.

Respectfully submitted,

ALBERT C. HALE,

General Secretary.

BROOKLYN, N. Y., December 26, 1894.

## FINANCIAL REPORT OF GENERAL SECRETARY OF AMERICAN CHEMICAL SOCIETY.

DECEMBER 1, 1894.

Dues collected for the year 1892 .....	\$	15.00	
" " " " 1893 .....		193.00	
" " " " 1894 .....		2,851.00	
" " " " 1895 .....		105.00	
Interest received on bank deposit.....		5.73	\$3,169.73
Commissions deducted, 10% on \$3,162.50.....		316.25	
Remitted to Treasurer.....	\$2,655.00		
Balance in bank, December 1, 1894.....	198.48	2,853.48	
Total receipts .....			\$3,169.73
Commissions deducted, 10% on \$3,162.50.....		316.25	
Amount due Treasurer:			
Account rebate to Local Sections .....	\$30.33		
Commission overdraft F. W. Traphagen.....	.15	30.48	



Commission due General Secretary from dues received by Treasurer on General Secretary's account, 10% on \$20.00.....	2.00	
Balance due Treasurer from General Secretary...		28.48
Net commission of General Secretary .....		\$287.77

After this the Treasurer's report was read by the Secretary and adopted, it having been previously audited by the Finance Committee.

## AMERICAN CHEMICAL SOCIETY.

### TREASURER'S REPORT FOR 1894.

#### *Receipts.*

Balance on hand, December 22, 1893.....	\$	74.05
Dues collected by Treasurer.....		622.09
Net dues and interest received from Secretary.....		2,853.48
Net commissions returned by Secretary .....		28.48
Cash received for subscriptions to Journal.....		575.42
"    "    " back numbers .....		159.48
"    "    " advertisements in Journal.....		131.80
"    "    " cancelled insurance policy .....		31.64
"    "    " Furniture sold to University C. N. Y.....		100.00
		<u>\$4,576.44</u>

#### *Disbursements.*

Expense of Journal and editorial office .....	\$2,890.27
"    " Secretary's office .....	413.12
"    " Treasurer's office.....	24.72
"    " Librarian's office .....	153.50
"    " Baltimore meeting (balance) .....	4.50
"    " Brooklyn meeting.....	60.55
General expense.....	16.50
Insurance.....	84.00
Rebate paid to Treasurer of N. Y. Local Section .....	200.00
"    "    "    " Washington Section.....	101.67
"    "    "    " Rhode Island Section.....	28.33
"    "    "    " Cincinnati Section.....	63.33
"    "    "    " Lehigh Valley Section .....	30.00
Balance on hand Dec. 22, 1894, in Bank of Metropolis, \$505.19	
Postage stamps.....	.76
	<u>505.95</u>

\$4,576.44

CHAS. F. MCKENNA, *Treasurer.*

No bills or claims, presented up to date and audited, remain unpaid.  
Accounts examined and found correct, E. and O. E.

A. P. HALLOCK,  
DURAND WOODMAN,  
FRANK T. KING,

New York, Dec. 22, 1894.

*Finance Committee.*

Professor Edward Hart, Editor of the Society's publications, gave an oral report showing what had been done in connection with the publication of the Journal of the Society, and explained how the scope of the Journal could be widened and that periodical maintained at the highest standard of excellence.

The report of the Librarian was then called for, but as the Librarian was absent and no report had been sent in, Professors A. H. Sabin, of Long Island City, and Wm. McMurtrie, of New York, presented informal statements of the condition of the library. Upon the request of the President, the report of the Librarian was ordered to be spread upon the minutes when it should be received by the Secretary.

The Society then proceeded to the order of general business, and, upon the motion of Professor A. C. Hale, adopted the following:

*Resolved*, That the General Secretary of the American Chemical Society is hereby authorized and requested, to take such steps as may be necessary to secure the passage of a bill by the Legislature of the State of New York, which shall so change the statutes of said State as to allow the Society to choose its Directors without regard to their being residents of the State of New York, or of any other state or locality.

The arranged program was then taken up, and a paper entitled "Note on the Estimation of Iron and Alumina in Phosphates," by K. P. McElroy, was read by the General Secretary. Dr. Thos. M. Drown then followed with a description of the Lawrence Experiment Station of the Massachusetts State Board of Health, and the nature of the work which was carried on there for the purification of the sewage and water. He distributed among the chemists present, copies of two tables showing methods and results of the experiments of the Station. Dr. Drown mentioned four methods of filtration in use, that had been tried at the Experiment Station; namely, rapid filtration through gravel, aided by a current of air, chemical precipitation, sedimentation, and straining through coke. The result obtained through the first system was particularly valuable; no other method had been found so capable of rapidly purifying a large amount of sewage. By means of this method some six or seven hundred thousand gallons were purified daily, and the effluent

rendered as wholesome as ordinary spring water. Dr. Drown then spoke of the results which had followed the purification of the drinking water and pronounced them marvelous. In Lowell and Lawrence the death-rate from typhoid fever had been three times greater than the normal. The inhabitants were mostly operators in mills and obtained their drinking water from the Merrimac river, which was contaminated by the sewage of the cities and towns along its course; since the purification of the water by rapid filtration through gravel, the death-rate and number of cases from typhoid fever had been diminished to an unprecedented degree. The money for these experiments had been appropriated by the State of Massachusetts, and the result justified the confidence placed in the State Board of Health and its experiments. After some questions and discussions upon Dr. Drown's remarks, a paper entitled, "The Coloring Matter in California Red Wines," was read by W. D. Bigelow.

Two papers were read by title; namely, "An Examination of the Atmosphere of Cleveland, Ohio," by C. F. Mabery, and "Rainfall and Typhoid Fever," by Wm. P. Mason, Troy, N. Y.

Mr. J. O. Handy then read a paper on "The Advantages in the Use of Barium Hydrate Solution as an Absorbent in Carbon Determination in Steel."

After this Professor C. E. Munroe read a paper by J. E. Blomen, on "Some Practical Points on the Manufacture of Nitro-Glycerine," and a paper by himself upon "Tellurium from Copper Residues," and exhibited an ingot of tellurium prepared in the laboratory of the Columbian University, which is believed to be the largest specimen of that metal ever obtained. The ingot was about six inches in length, one and one-half inches in width, and something more than one-fourth of an inch in thickness, showing beautiful metallic luster and crystalline formation; it weighed 16.7 ounces; at the quoted price of this element the value of the ingot would be something over \$250.

Professor Munroe then presented a paper, by Cabell Whitehead, on "The Estimation of Tellurium in Copper Bullion, and Professor Edward Hart read a paper entitled "Some Points in the Distillation of Nitric Acid." After some announcements, the Session adjourned at 1 P. M.

Upon the adjournment of the Session the chemists went directly to the Union Station, at Causeway St., where lunch was served by the Local Committee.

The weather having become fairly pleasant, it was decided here to take the train for Malden, after lunch, and visit the manufactory of the Boston Rubber Shoe Company, at Fells Station. Arriving at this destination, the chemists were very cordially received by the Superintendent, Mr. Robson, who escorted the party to the various departments in the building, carefully explaining to them all details of the various processes. They were shown first the washroom, where crude rubber from Para, Central America, and Africa, was sheeted and cleaned by running through the heavy rollers with a current of water pouring down upon it; next they were taken to the drying lofts, where the sheeted rubber is left for a few days exposed to the air at a temperature of 80°-90° F.; from this place the rubber is taken to the mixing room, where it is again run through heavy rollers, each having a different rate of speed; a mixture of vulcanizing agents (sulphur and litharge), coloring matter (lamp-black), inert filling (whiting), and reclaimed rubber and coal tar is then thrown upon the sheeted rubber as it passes between the rollers, which by their different rates of speed produce an effect like the kneading of dough, so that the material is thoroughly intermixed with the rubber, forming a homogeneous mass. The stock thus prepared is soft and extremely adhesive, its surfaces uniting firmly and permanently by contact and pressure. For convenience in handling, its adhesiveness can be temporarily removed by dusting the surfaces with flour, talc, etc.

The sheets formed by passing this material between the rollers can be prevented from sticking together by interposing plain sheeting for wrapping cloth, and they are transferred to the cutting room on cloth frames. All of the cutting is done on wooden blocks or zinc surfaces; the different methods of cutting are: *a.* Hand-knife and metal template. *b.* Hand die and mallet. *c.* Machine die. *d.* Machine knife (soles only). Fabrics are cut several thicknesses at once; sheet rubber singly.

Engraved surfaces, such as uppers and soles for rubber shoes, are made by passing the sheet rubber between rollers having

corresponding figures. Throughout all the processes of manufacture, except the making of heels, the rubber remains unvulcanized until everything else is done, vulcanization being the last step of all. Heels for heavy overshoes are made by hydraulic steam-jacketed presses, which form and vulcanize them at the same time.

In the boot and shoe rooms proper, the operations are as follows: *a.* Lasting innersole and lining over maple last. *b.* Applying the stay pieces, straps, etc. *c.* Covering outside with cloth or rubber upper. *d.* Attaching the soles. Each part requires to be rolled in place to insure adhesion and perfect contact. All dry surfaces are brushed over with rubber cement (solution of rubber compound in naphtha). Such goods as are to have a bright finish receive a coat of thin linseed-oil varnish previous to vulcanization.

The completed goods containing the lasts are vulcanized on iron cars, in chambers heated by steam coils. Temperature, 260°–270° F. Time, six to seven hours. The temperature is equalized and the volatile products removed by ventilation.

After vulcanization the lasts are removed and the boots and shoes packed for shipment.

#### SECOND DAY'S SESSION.

The meeting was called to order at 10.15 A. M. in the Chemical Lecture Room, Boylston Hall, Harvard University, Cambridge, Mass.

Professor C. Loring Jackson welcomed the chemists to Cambridge and the University; he described the location and arrangement of the various laboratories, museums, etc., which would be open for inspection after the morning session. President Wiley made some very appropriate remarks in response, after which the following papers were read:

Methods for the Examination of Glycerine for use in the Nitro-Glycerine Manufacture, by G. E. Barton. Read by title.

Report of the Committee on Atomic Weights for 1894, by F. W. Clarke. Read by the Secretary.

The Volumetric Determination of Phosphorus in Steel, by W. A. Noyes and J. S. Royse. Read by C. B. Dudley.

Note on the Manufacture of Zein, by A. H. Sabin.

The Volumetric Determination of Orcin, by H. S. Neiman.  
Read by title.

Note on the Purification of Glucinum Salts, by Edward Hart.

The Estimation of Sulphur in Pyrites, by George Lunge.  
Read by Edward Hart.

Some New Forms of Extractive Apparatus, by A. E. Knorr.  
Read by title.

Recent Work on the Atomic Weight of Oxygen, by E. W. Morley.

After Professor Morley's paper the Committee of Canvassers made their report, and the President announced the result of the annual election, which was as follows:

*President*—Edgar F. Smith, Philadelphia.

*General Secretary*—Albert C. Hale, Brooklyn.

*Treasurer*—C. F. McKenna, New York.

*Librarian*—F. E. Dodge, Brooklyn.

*Directors* (to serve two years)—H. W. Wiley, Washington; Wm. McMurtrie, New York; J. H. Appleton, Providence; A. A. Breneman, New York.

*Councilors*—(to serve three years)—F. W. Clarke, Washington; W. L. Dudley, Nashville; E. R. Squibb, Brooklyn; G. F. Barker, Philadelphia.

Upon the motion of Edward Hart, the Society unanimously passed a vote of thanks to the following individuals and corporations for courtesies received: Corporation and Faculty of the Massachusetts Institute of Technology; also Corporation of Harvard University; Dr. Thos. M. Drown; Professor C. Loring Jackson; Professor H. B. Hill; to the Boston Rubber Shoe Co., and Superintendent Robson; Authorities of the State Experiment Station at Lawrence, Mass., and members of the Associated Press. The address of the retiring President, "The Synthetic Food of the Future," was then presented by H. W. Wiley. At the close of the address, Dr. Wiley reviewed the history of the Society during the two years of his presidency, and expressed his thanks to the members, and especially to the various officers of the Society, who had aided him in making such marked advancement in numbers, in the character of the work and publications, and in the general reputation which the Society had gained throughout the world.

The Society then adjourned its session, and the chemists were tendered a lunch at the Colonial Club. The remainder of the

day was spent in examining the various laboratories, museums, and collections of the University.

The following named persons were registered in attendance at the meeting:

H. W. Wiley, Washington, D. C.  
 Edward Hart, Easton, Pa.  
 Albert C. Hale, Brooklyn, N. Y.  
 Charles L. Parsons, Durham, N. H.  
 Chas. W. Moulton, Poughkeepsie, N. Y.  
 C. H. White, Naval Laboratory, Brooklyn, N. Y.  
 T. M. Drown, Mass. Inst. Tech., Boston, Mass.  
 Chas. B. Dudley, Altoona, Pa.  
 Wm. McMurtrie, 106 Wall St., New York City.  
 Ellen H. Richards, Boston, Mass.  
 Arthur A. Noyes, Boston, Mass.  
 Augustus H. Gill, Mass. Inst. of Tech., Boston, Mass.  
 Walter S. Allen, Boston Gas Light Co., Boston, Mass.  
 William K. Robbins, Manchester, N. H.  
 Charlotte A. Bragg, Wellesley, Mass.  
 Mary E. Mathews, Painesville, Ohio.  
 Henry P. Talbot, Mass. Inst. Tech., Boston, Mass.  
 Walter L. Jennings, Boston, Mass.  
 Thomas Evans, Mass. Inst. Tech., Boston, Mass.  
 S. Lawrence Bigelow, Boston, Mass.  
 William T. Hall, 222 Marlborough St., Boston, Mass.  
 Rolfe M. Ellis, Hyde Park, Mass.  
 Chas. H. Miller, Baltimore, Md.  
 Chas. T. Pomeroy, Newark, N. J.  
 Durand Woodman, New York City.  
 Walter M. Saunders, Olneyville, R. I.  
 H. J. Wheeler, Kingston, R. I.  
 W. D. Bigelow, Washington, D. C.  
 Walter E. Smith, Providence, R. I.  
 Jas. O. Handy, Pittsburg, Pa.  
 Herbert L. Lamborn, Alliance, Ohio.  
 Henry H. Tozier, Haverhill, Mass.  
 Chas. W. Hapgood, Everett, Mass.  
 E. H. Laws, Bedford, Mass.  
 Sidney S. Emery, Philadelphia, Pa.  
 David B. Weston, Sharon, Mass.  
 Charles A. Meserve, Allston, Boston, Mass.  
 Albert Dunbar, Pittsfield, Mass.  
 C. Tennant Lee, Boston, Mass.  
 Bennett F. Davenport, Boston, Mass.

Edward W. Morley, Cleveland, Ohio.  
Charles E. Munroe, Washington, D. C.  
J. M. Crafts, Inst. of Technology, Boston, Mass.  
J. H. Long, Chicago, Ill.  
Severance Burrage, Inst. of Technology, Boston, Mass.  
Frederick W. Howe, Durham, N. H.  
Lewis H. Kittredge, Durham, N. H.  
Charles A. Pitkin, South Braintree, Mass.  
Charles A. Catlin, Providence, R. I.  
George F. Andrews, Providence, R. I.  
John H. Washburn, Kingston, R. I.  
J. F. McGregory, Hamilton, N. Y.  
J. W. Ellins, Framingham, Mass.  
S. P. Sharples, Boston, Mass.  
Walter Woodman, M.D., Cambridge, Mass.  
A. H. Sabin, Long Island City, N. Y.  
Albert M. Todd, Kalamazoo, Mich.  
W. P. Cutter, Washington, D. C.  
Howard C. Saunders, Providence, R. I.  
Leonard P. Kinnicutt, Worcester, Mass.  
Edw. P. Harris, Chester, Pa.  
John B. Stearns, University of Vermont.  
W. R. Orndorff, Ithaca, N. Y.  
R. P. Williams, Boston, Mass.  
Thomas B. Osborne, New Haven, Conn.  
W. R. Livermore, Boston, Mass.  
John F. Bannan, North Andover, Mass.  
Horace A. Bishop, Providence, R. I.  
Fred. L. Thayer, Providence, R. I.  
Frank N. Smalley, Westboro, Mass.  
S. D. Gage, Mass. Inst. Tech., Boston, Mass.  
Harris E. Sawyer, Cambridge, Mass.  
George Oenslager, Harrisburg, Pa.  
Martin H. Ittner, St. Louis, Mo.  
Frederick L. Dunlap, Chillicothe, Ohio.  
Delia M. Stickney, Cambridge, Mass.  
C. Belle Kenney, East Boston, Mass.  
G. C. Hodges, Utica, N. Y.  
A. E. Dolbear, Tufts College, Mass.  
C. L. Jackson, Cambridge, Mass.  
H. B. Hill, Cambridge, Mass.  
Fred. W. Morse, Durham, N. H.  
W. B. Lindsay, Dickinson College, Carlisle, Pa.  
Stephen Freeman, Boston, Mass.



### COUNCIL.

The bill for printing the December number of the JOURNAL, amounting to more than \$250, it was submitted to the Council according to the Constitution, and approved by them January 5, 1895.

#### NEW MEMBERS ELECTED DECEMBER 26.

Becher, Jesse B., Lincoln, Neb.  
Brown, Lucius P., Nashville, Tenn.  
Chase, Geo. W., Phillipsburg, N. J.  
Franklin, Edward Curtis, Lawrence, Kan.  
Grindly, Dr. H. S., East Green St., Champaign, Ill.  
Harrison, Herbert E., B.S., Agricultural College, Mich.  
Hiltner, Robert S., Lincoln, Neb.  
Meeker, G. H., Longdale, Va.  
Miller, Hugh L., Wilmington, N. C.  
Nelson, E. K., 6814 Union Ave., Englewood, Ill.  
Nicholson, Edward E., Lincoln, Neb.  
Rossman, William L., B.S., Agricultural College, Mich.  
Wardman, Geo. B., care of Detroit Copper Company, Morenci, Ariz.  
White, A. H., West University Ave., Champaign, Ill.  
White, John, Ph.D., Lincoln, Neb.

#### ELECTED JANUARY 12.

Barrows, W. A., Jr., Sharpsville, Pa.  
Beeson, J. L., care Audubon School of Sugar, Audubon Park, New Orleans, La.  
Billings, Edgar F., 165 High St., Boston, Mass.  
Fassett, Chas. M., Spokane, Wash.  
Frohman, Edward D., 68 W. Third St., Cincinnati, Ohio.  
Graham, Robert O., Bloomington, Ill.  
Guess, George A., M.A., Fairview via. Penticton, B. C.  
Homburg, Fred., 40 Clifton Ave., Cincinnati, Ohio.  
Loewenstein, Harry, 144 Hackberry St., Cincinnati, Ohio.  
Mather, Henry A., 27 Pierrepont St., Brooklyn, N. Y.  
Neher, Fred., Princeton, N. J.  
Peyton, William C., care The Cal. Powder Works, Santa Cruz, Cal.  
Roth David M., 36 Ingleside Place, Cincinnati, Ohio.  
Shaw, Professor G. W., Corvallis, Benton Co., Oregon.  
Smith, J. D. Audley, Clifton, Ariz.  
Swenson, M., Monadnock Block, Chicago, Ill.  
Thorburn, A. D., 465 State St., Chicago, Ill.  
Tucker, Francis F., Nebraska City, Neb.  
Wrampelmeier, Theodore J., Custom House, San Francisco, Cal.

ELECTED JANUARY 17.

Freeman, Stephen, 79 Montgomery St., Boston, Mass.  
Guild, Frank N., Greenboro, Vt.  
Johnson, Emil F., 96-98 Maiden Lane, N. Y. City.  
Miller, Edmund H., Ph.D., 41 East 49th St., N. Y. City.  
Newell, H. E., Saxtons River, Vt.  
Pickert, Lee W., Amer. Sugar Ref. Co., Granite St., South  
Boston, Mass.  
Redding, Allen C., Findlay, Ohio.  
Spaulding Edward G., 43 W. 32nd St., N. Y. City.  
Worcester, Charles P., State House, Boston, Mass.

ASSOCIATE ELECTED JANUARY 17.

Fosdick, Eugene H., San Diego, Cal.

CHANGES OF ADDRESS.

Barton, G. E., Hatfield, Mass.  
Catlin, Chas. A., 133 Hope St., Providence, R. I.  
Clarke, F. W., U. S. Geological Survey, Washington, D. C.  
Dickerson, E. N., 253 Broadway, N. Y. City.  
Dudley, Chas. B., Drawer 334, Altoona, Pa.  
Eichberg, Julius H., M.D., 50 West 9th St., Cincinnati, Ohio.  
Hahn, A. G. C., care of Nepera Chemical Company, Nepera  
Park, N. Y.  
Jackson, C. E., care of Wm. S. Merrell Chemical Company,  
Cincinnati, Ohio.  
Kedzie, Frank S., 414 Ottawa St., Lansing, Mich.  
Lanning, John G., care of Cleveland R. M. Company, Cleve-  
land, Ohio.  
Latham, Woodville, Hotel Bartholdi, Madison Square, N. Y.  
City.  
Randolph, R. B. F., Hoagland Laboratory, Brooklyn, N. Y.  
Smith, Herbert E., Yale Medical School, New Haven, Conn.  
Wardman, Geo. B., care of John L. Elliot, Ahualulco, Estado  
de Jalisco, Mexico.

ADDRESSES WANTED.

Davis, G. C., old address, 311 W. Mahantonga St., Potts-  
ville, Pa.  
Ray, Victor, old address, Anaconda Electrolytic Refinery,  
Anaconda, Montana.

## MEETINGS OF THE SECTIONS.

## WASHINGTON SECTION.

Thursday, December 13, 1894.

The Society was called to order at 8 P. M. by the President, Dr. Seaman, with twenty members present. The minutes of the 76th meeting were read and approved.

The first paper of the evening was read by Mr. Carr on "The Dehydration of Viscous Organic Liquids," by Oma Carr and F. T. Sanborn.

The authors reviewed briefly the various accepted methods for the dehydration of organic liquids, noting the peculiarly conflicting statements of authorities regarding oxidation and decomposition during heating. Statements of Jungfleisch and Lefranc, Dieck and Tollens, Battmann, and others are not in accord regarding the decomposition of levulose at various temperatures.

The authors discussed the essential factors of the ideal dehydration method, stating these to be: (1) Homogeneity of liquids. (2) Uniform distribution of small quantities over large surfaces. (3) Uniform temperature. (4) Rapidity of dehydration.

"It has been found that as these conditions have been more perfectly attained, results have been more generally concordant. It may be said that, given a homogeneous liquid and uniformity of temperature, the method which insures wider distribution will provide greater rapidity of drying. Inasmuch as at a given temperature, alteration of the material will be proportionate to the time, results closer to the truth will be afforded by the method accomplishing the drying in shorter period."

The method devised by the authors is in accord with the above principles, and has been applied, so far, to the following range of materials: Heavy sorghum molasses, mixtures of sugar and levulose, milks, cream, maize juice (22 years old), beet juices, honies, sorghum juices, commercial glucoses, and rosin turpentine solutions. The work on these materials covers over 4,000 determinations, in which the maximum variation in quadruplicates was 0.09 per cent., minimum 0.0, and mean 0.057 per cent. These results were obtained in from two to four hours, according to the character of the material.

The method is based upon the porosity of pumice stone, the

latter being crushed into fragments the size of a pea, strongly ignited, cooled, and the liquid to be dried, weighed from a pipette-weighing bottle, and uniformly distributed over the stone. The drying is conducted as usual.

The authors reserve the details of the method for future papers, work of a more complex character being now under way.

#### *Discussion.*

Professor Wiley said the method had been proved accurate in giving duplicate results, although agreement is not proof of accuracy. The method could be used to determine matters volatile at 100°, chiefly water, as can be proved by passing them through sulphuric acid. Many of the substances to be dealt with contain levulose, and it is remarkable that we don't know just what takes place upon drying it, as the most opposite statements have been made. The determination of water is one of the most difficult things in agricultural chemistry, and this method is a step in advance. He referred to the fact that by the use of aluminum, flat dishes of wide expanse can be obtained.

Mr. Cutter stated that he had used practically the same method in the Utah Station, except that he had used the Hoffmeier capsules, and that the material, after being dried, could be utilized in other ways, especially the determination of fats in the analyses of meats. In his opinion, correct sampling of green material and the correct determination of moisture in original samples was, at present, one of the most perplexing problems with which agricultural chemists have to deal.

Professor Wiley said that green fodders should be shredded. The Laboratory of the Agricultural Department has the only shredding machine in the United States and it furnishes a good pulp.

Professor Seaman asked if the idea was to obtain a sufficient surface of pumice stone and was answered affirmatively.

W. D. Bigelow and E. E. Ewell called attention to a continuous extractor for large quantities of material. The apparatus consists of a percolator with slightly diverging sides, supported by an iron tripod, which in turn is placed in a shallow tray of enameled iron, or some other material which is not attacked by mercury. A crystallizing dish is placed below the percolator, and a bell-jar, with a reflux condenser attached, is placed over

the percolator, with its edges resting on the tray. The tray is then partially filled with mercury to prevent the escape of the ether.

January 10, 1895.

President W. H. Seaman in the chair; 14 members present; The following officers were elected:

*President*—Chas. E. Munroe.

*Vice-Presidents*—E. A. de Schweinitz and W. D. Bigelow.

*Treasurer*—W. P. Cutter.

*Secretary*—A. C. Peale.

*Additional Members of Executive Committee*.—H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman.

#### CINCINNATI SECTION.

December Meeting.

Messrs. W. G. Wallace, Richard W. Proctor, George F. Feid, and Charles E. Jackson were elected to membership in the Section.

The election of officers for 1895 resulted as follows:

*President*—Karl Langenbeck.

*Vice-Presidents*—B. D. Westenfelder, and Irwin J. Smith.

*Treasurer*—Henry B. Foote.

*Secretary*—E. C. Wallace.

*Directors*—Dr. S. P. Kramer, Professor O. W. Martin, and H. L. Nickel.

Papers were read by Dr. S. P. Kramer on "Diphtheria Antitoxin," and Dr. Alfred Springer on "Elective Fermentation in Diabetes."

The following resolution was adopted:

*Resolved*, That the Cincinnati Section of the American Chemical Society respectfully recommends to the Committee on Nomenclature and Spelling of the JOURNAL of the Society, the use of the rules concerning the spelling of chemical terms recently adopted by the American Association for the Advancement of Science, limiting, however, the application of the rule concerning the spelling of *gramme* to articles in the field of medical or pharmaceutical chemistry.

Tuesday, January 15, 1895.

Vice-President Westenfelder in the chair.

Mr. F. Homburg and E. D. Frohman, recently elected members of the American Chemical Society, were elected to membership in the Section.

Mr. E. Twitchell read a paper on "The Separation of Solid and Liquid Fatty Acids." After reviewing the different methods of analysis of fats, Mr. Twitchell stated, that in his opinion, by precipitating all the solid and part of the liquid fatty acids from alcoholic solution by lead acetate (Jean's method) and determining iodine in a number of both original fatty acids and liquid acids left in the alcoholic solution, by calculation therefrom the amount of saturated and unsaturated fatty acids present in the fat could be determined with a fair degree of accuracy.

Dr. H. E. Newman read a "Report of Progress in Organic Chemistry," touching briefly upon L. Gatterman's method of reducing aromatic nitro compounds by a current of electricity; B. Tollens' work on the birotation of glucose; the synthesis of polyhydric alcohols by B. Tollens, H. Hosaus, and others, and Trillat's method of manufacturing dyes from formaldehyde and several amines, etc.

Reports of the Treasurer and Secretary, for 1894, were read and adopted. The Secretary's report showed an increase of six in membership, and that twenty papers had been read at the eight meetings held during the year.

#### LEHIGH VALLEY SECTION.

Thursday Evening, January 17, 1895.

The annual meeting was held at the Franklin House, Easton, Pa., six being present. A pleasant social time was spent, the only business transacted being the election of officers for the coming year. Messrs. Green and Brinker acted as tellers, and reported, on opening the ballots, the election of the following:

*Presiding Officer*—Edward Hart.

*Secretary*—Albert H. Welles.

*Treasurer*—Albert L. Colby.

*Executive Committee*—George P. Scholl, and J. W. Richards.

## Proceedings.

### COUNCIL.

January 23, 1895, the following resolution was approved by a majority of the Council:

*Resolved*, That the salary of the Editor for the year 1895 be fixed at two hundred and fifty dollars (\$250).

### CHANGES OF ADDRESS.

Blonin, R. E., 700 North St., Baton Rouge, La.  
Couch, Guy E., Swissvale, Allegheny County, Pa.  
Ewell, E. E., 2227 Fifteenth St., N. W., Washington, D. C.  
Field, Walter D., 4 Cedar St., New York City.  
Hahn, A. G. C., Nepera Chemical Co., Nepera Park, N. Y.  
Leighton, Virgil F., 1128 Ohio St., Lawrence, Kas.  
Marshall, G. D., 52 Cheshire St., Cleveland, Ohio.  
Miller, Chas. H., care of Baltimore Electric Refining Co.,  
Keyser Building, Baltimore, Md.  
Redwood, Dr. Boverton, 4 Bishopgate St., Within, London,  
E. C., England.  
Weems, J. B., Iowa Agricultural College, Ames, Iowa.  
Wickhorst, Max, 2421 Dearborn St., Chicago, Ill.  
Williams, W. J., 635 Market St., Camden, N. J.

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### MEETINGS OF THE SECTIONS.

#### CINCINNATI SECTION.

*Discussion of paper by E. Twitchell, read January 15, 1895.*

Dr. Newman asked Mr. Twitchell if he had ever mixed the pure solid and liquid fatty acids in the same proportion in which they were thought to exist in a given fat, and determined whether or not the iodine number of the mixture agreed with that of the fat.

Mr. Twitchell replied that he never had; he thought it was a good idea, but it was very difficult to obtain the liquid acids pure, and if obtained pure, on the slightest exposure to air, they would become more or less oxidized.

Replying to the question whether oleic acid could be obtained

pure, Mr. Twitchell said all fats contained linolic acid ; he had never found a fat which contained oleic acid free from linolic.

Professor Lloyd stated that he had once tried this separation of solid and liquid fatty acid by Muter's method. His experience led him to believe that lead stearate and palmitate were soluble in the lead oleate, and this mixture was soluble in ether. While pure lead stearate and palmitate might be nearly or quite insoluble in ether, in the presence of the oleate, ether would dissolve an appreciable amount. He would like to know what Mr. Twitchell considered the so-called pure oleic acid of the market to be.

Mr. Twitchell replying, said it was probably oleic acid with some oxidized acids.

Professor Lloyd then asked whether any method by means of which ten per cent. of cottonseed-oil could be detected in olive-oil existed.

Mr. Twitchell replied that he would not be positive about ten per cent., thought possibly twenty per cent. could be detected ; he said the difficulty was due to the fact that oils contain all the fatty acids in different proportions, that two samples of pure oil might vary as much as the mixtures, so far as chemical composition was concerned they were the same.

Mr. Smith remarked that Dr. Stuerke had carried on a series of experiments for over a year, and had found that he could not differentiate less than ten per cent. of oils. Artificial lards are made on this basis.

Mr. Twitchell said that by treating a sample of olive-oil known to be pure, and an adulterated oil with sulphuric acid of given strength, he thought, after some practice, one ought to be able to detect five per cent. of cottonseed-oil.

#### RHODE ISLAND SECTION.

The regular monthly meeting of the Section was held at Providence, January 17, 1895.

President Charles A. Catlin in the chair.

Mr. Geo. F. Andrews read a paper upon The Accuracy of the Fine Assay of Silver.

The paper briefly discussed the general inaccuracy of the fine assay of silver, and the difficulty of getting a satisfactorily accurate assay of ores by the methods now in use.

It also discussed, in some detail, the losses in cupelation due to absorption and to volatilization. The effect upon the button of too great heat and too large amount of lead.

Mr. E. D. Pearce gave an interesting account of the use of hydrocyanic acid in destroying insects upon trees.



## Proceedings.

### COUNCIL.

The following persons have been elected by the Council to serve on the various standing committees for the coming year:

Committee on Nominations to Membership.—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Committee on Finance.—Durand Woodman, A. P. Hallock, and A. H. Sabin.

Committee on Papers and Publications.—J. H. Long and E. F. Smith. Professor Smith desiring to be relieved from duty on this committee, the Council has elected Thomas B. Osborne to the vacancy.

Springfield, Mass., has been chosen as the place for the summer meeting.

### NEW MEMBERS ELECTED FEBRUARY 5.

Chesnut, V. K., Bio-Chemic Laboratory, U. S. Department of Agriculture, Washington, D. C.

Cobleigh, Wm. M., E.M., Agricultural College, Bozeman, Mont.

Desper, Ernest W., 37 Shelby St., Worcester, Mass.

Fields, J. W., 88 Wall St., New York City.

Lotz, Dumont, Portland, Ind.

Marshall, Geo. D., care of Newport Mining Co., Ironwood, Mich.

Murray, C. B., Braddock, Pa.

Penniman, Russell S., Lock P. O. Box 26, Dover, N. J.

Perry, Joseph H., 176 Highland St., Worcester, Mass.

Robbins, William K., Amoskeag Manufacturing Co., Manchester, N. H.

Rosengarten, Dr. Geo. D., 17th and Fitzwater Sts., Philadelphia, Pa.

Schloss, Joseph A., care of La Gran Fundision Nacional Mexicana, Monterey, Mexico.

Thiry, Joseph, care of Dr. G. E. Moore, 221 Pearl St., New York City.

Todd, Albert M., Kalamazoo, Mich.

Viall, William A., Brown and Sharp Manufacturing Co., Providence, R. I.

Woods, Henry, Wellesley, Mass.

#### ELECTED MARCH 1.

Bogardus, C. E., 60 Columbia St., Seattle, Wash.

Carlsson, Hugo, care of The Johnson Co., Johnstown, Pa.

Cox, W. Wetherill, 2025 Westmoreland St., Tioga, Phila.

Dobbin, Leonard, Chemistry Department, University of Edinburgh.

Dorset, Marion, Bio-Chemic Laboratory, Department of Agriculture, Washington, D. C.

Ehrenfeld, Augustus C., 15 West Monument Ave., Dayton, Ohio.

Ellis, G. H., Metropolitan Block, Chicago, Ill.

Jones, L. J. W., 1821 Arapahoe St., Denver, Col.

Keller, Charles, Wilkinsburg, Pa.

Mixer, Chas. T., 600 East High St., Ishpeming, Mich.

Thompson, Elihu, Lynn, Mass.

Tompkins, Vreeland, 553 Communipaw Ave., Jersey City, N. J.

Wagner, William G., 101 Leadenhall St., London, E. C., England.

#### ASSOCIATE ELECTED FEBRUARY 5.

Reubens, Charles M., 77 East 115th St., New York City.

#### CHANGES OF ADDRESS.

Coombs, Frank E., Natick, Mass.

Dewey, F. P., 621 F St., Washington, D. C.

Dodge, F. E., Box 85, Long Island City, N. Y.

Enequist, John, 136 Liberty St., New York City.

Hancock, David, Park View, Portsmouth, Va.

Stone, Edward P., Experiment Station, Durham, N. H.  
Townsend, Clinton, Barton P. O., La.  
Wrampelmeier, T. J., 909 Steiner St., San Francisco, Cal.

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## MEETINGS OF THE SECTIONS.

### CINCINNATI SECTION.

February 15, 1895.

Dr. Alfred Springer in the chair.

A communication was read from Mr. John H. Westenhoff, stating his inability to be present, on account of a severe cold, and asking to have his paper on "Determination of Phosphorus in Ferro-Silicon" postponed to next meeting.

Professor Norton then stated that Mr. Robert Hochstetter, who was to read a paper on "The Souring of Milk," was detained at home by the serious illness of his business associate, Mr. L. W. Hoffman, and his paper would also have to be postponed.

Professor J. U. Lloyd spoke of the difficulty of obtaining distilled water which would meet the requirements of the U. S. Pharmacopeia, and described the apparatus he was having made consisting of a large copper still, a stone worm forty feet in length, and a stone receiver with stone stop-cock.

Dr. Springer said that absolutely pure distilled water could not be obtained in large quantities for technical use.

Professor Norton told of some interesting experiments carried on at the Laboratory of the University of Cincinnati, for the past five months, to determine the relative value of condensing-tubes made of block tin, aluminum, and glass. He said all glass was affected by water at high temperatures, and water distilled from glass vessels must, necessarily, be more or less contaminated; aluminum, owing to its high conductivity, made an excellent condensing-tube, and did not seem to be affected by water. Condensing-tubes of aluminum could also be used for distilling alcohol, ether, and many other liquids.

Chairman of Standing Committees were elected as follows:

Didactic, Physical, and Inorganic Chemistry, Dr. Alfred Springer, Chairman.

Organic Chemistry, Professor T. H. Norton, Chairman.

Analytical Chemistry, Lewis W. Hoffman, Chairman.

Medical, Physiological, and Biological Chemistry, Dr. S. P. Kramer, Chairman.

Technical and Pharmaceutical Chemistry, Professor J. U. Lloyd, Chairman.

On motion it was—

*Resolved*, That this Section respectfully recommend to the Committee on Publication of the Journal, the eminent desirability of having the leaves of the Journal cut before being sent to the members of the Society, as is the rule with the publications of the London Chemical Society and the Society of Chemical Industry.

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RHODE ISLAND SECTION.

The regular monthly meeting was held at Providence, on the evening of February 23rd. Mr. Frank H. Andrews in the chair. Professor J. H. Appleton read a paper on Argon, presenting the facts as now known, and certain suggestions arising from them.





*H. B. Nason*

## Proceedings.

### BOARD OF DIRECTORS.

A charter for a Chicago Local Section was granted March 15.

### NEW MEMBERS ELECTED MARCH 22.

Catlett, Charles, 10 New Court House St., Staunton, Va.  
Frissell, W. I., 52 14th St., Wheeling, W. Va.  
Griffith, H. E., Oak Park, Cook County, Ill.  
Sharwood, W. J., University of California, Berkeley, Cal.  
Wait, Prof. Chas. E., Ph.D., University of Tennessee, Knoxville, Tenn.  
Williamson, G. N., 14 Dey St., N. Y. City.

### CHANGES OF ADDRESS.

Carlsson, Hugo, care of The Johnson Company, Lorain, Ohio.  
Clark, Dr. John E., 18 John R. St., Detroit, Mich.  
Couch, Guy E., 305 Mills St., Braddock, Pa.  
Guitermann, Franklin, 2815 Gilpin St., Denver, Colo.  
Hancock, David, care of Sloss Iron and Steel Company, Birmingham, Ala.  
Hazen, Allen, care of Noyes and Hazen, 85 Water St., Boston, Mass.  
Hoffmann, Philip C., care of The Chesapeake Guano Company, Equitable Building, Baltimore, Md.  
Howe, Frederic W., 9 Ashburton P. O., Boston, Mass.  
Keller, Chas., 113 Biddle Ave., Station D., Pittsburg, Pa.  
Simon, Dr. S. E., care of The Oscar A. Nenninger Company, Riverside Ave., near Second River, Newark, N. J.  
Waldcott, Dr. Sigmund, care of Messrs. Lloyd Bros., Court and Plum Sts., Cincinnati, Ohio.  
Weston, Robert Spurr, 21 Wyman St., Brockton, Mass.  
Wetmore, L. L., 35 Suffolk St., Holyoke, Mass.  
Zinsser, Fred. G., 197 William St., New York City.

## MEETINGS OF SECTIONS.

## CINCINNATI SECTION.

March 15, 1895.

Vice-President Irwin J. Smith presided.

A communication was read from the Globe Soap Company announcing the death of W. G. Wallace. The Secretary was instructed to express the sympathy of the Section to the family of the deceased.

Professor T. H. Norton then proposed the following resolution :

*Resolved*, That this Section of the American Chemical Society deplores the loss which it has suffered through the death of one of its most earnest and active members, Mr. Lewis William Hoffmann, Chairman of the Committee on Analytical Chemistry, which occurred at Cincinnati on March 4, 1895.

*Resolved*, That the Section expresses to the family of the late Mr. Hoffmann its deep sympathy with them in their sudden bereavement.

Mr. John H. Westenhoff read a paper on the "Determination of Phosphorus in Ferro-Silicon." Mr. Westenhoff had experienced great difficulty in dissolving ferro-silicons in nitric or hydrochloric acid or aqua regia. He found by adding a small quantity of hydrofluoric acid to either nitric or hydrochloric acid, solution could be readily effected, and the determination could then be carried on by the usual method. Very satisfactory results were obtained and the time was shortened to that required for phosphorus determinations in pig iron.

Mr. Robert W. Hochstetter read a paper on "The Souring of Milk." He ascribed the souring of milk to the presence of bacteria and showed the chemical changes that took place. Results of analyses of a sample of milk, a portion of which was analyzed each day for five days, showed the amount of total solids decreased, the per cent. of fat was constant, while the acidity was variable and not proportional to the length of time milk had been standing. Electric discharges, produced over the surface of the milk for several hours, seemed to have little or no effect, and Mr. Hochstetter thought the souring of milk during thunder storms was due to the fact that the atmospheric condi-



tions were more favorable to the growth of the bacilli. He found that milk cooled quickly, as soon as drawn from the mammary gland, was not liable to sour during thunder storms.

Mr. E. Twitchell was elected Chairman of the Committee on Analytical Chemistry to fill the vacancy caused by the death of Lewis W. Hoffmann.

#### WASHINGTON SECTION.

Thursday, February 14, 1895.

President Charles E. Munroe in the chair.

The meeting was devoted mainly to the address of the retiring President, Dr. Wm. H. Seaman. His subject was "Chemistry in Education," which was considered under four heads: (1) What is chemistry, (2) what are its relations to common life, (3) how much chemistry is actually taught in our schools, and (4) what should be taught there. After the delivery of the address, it was resolved to co-operate with the other scientific societies in enlarging the powers of the joint commission, and the adoption of a constitution for the joint commission based upon its being composed of the officers and administrative boards of the several component societies.

Thursday, March 14, 1895.

President Charles E. Munroe in the chair; thirty-five members present; Mr. G. E. Barton was elected to membership.

Professor F. W. Clarke gave a brief account of his general theory concerning the constitution of the silicates. His work will appear in full as a bulletin of the U. S. Geological Survey. Parts of it have already appeared in this JOURNAL.

Dr. H. N. Stokes read a paper on the "Chloronitrides of Phosphorus and the Metaphosphimic Acids." The paper was a contribution to the subject of homology and polymerism of inorganic compounds. It was shown that Liebig's chloronitride of phosphorus,  $P_3N_3Cl_3$ , is but one member of an homologous series of chloronitrides, having the general formula  $(PNCl_2)_x$ , two others of which were described; viz.,  $(PNCl_2)_1$ , and another of

unknown molecular weight. The chloronitrides ( $\text{PNCl}_2$ )<sub>3</sub> and ( $\text{PNCl}_2$ )<sub>4</sub>, by saponification, yield trimetaphosphimic acid, ( $\text{PNO}_2\text{H}_2$ )<sub>3</sub>, and tetrametaphosphimic acid, ( $\text{PNO}_2\text{H}_2$ )<sub>4</sub>, which may be regarded as members of an homologous series of acids parallel with the metaphosphoric acid series, and having one-third of the oxygen of the latter replaced by the amide group. These acids being derived from chlorides containing the nuclei ( $\text{PN}$ )<sub>x</sub> may be regarded as polymers of the simplest form  $\text{PNO}_2\text{H}_2$ , in which nitrogen atoms serve as connecting links between the phosphorus atoms.

Dr. J. E. Blomén read a paper "On the Manufacture of Soluble Nitrocellulose for Nitrogelatine and Plastic Dynamite."

## Proceedings.

### BOARD OF DIRECTORS.

A Charter for a Nebraska Local Section was granted April 15, 1895.

The following act was passed by the Senate and Assembly of New York, and approved by the Governor April 18, 1895:

#### CHAPTER 346.

##### *An Act for the Relief of the American Chemical Society.*

The people of the state of New York, represented in the Senate and Assembly, do enact as follows:

SECTION 1. It shall be lawful for the American Chemical Society to elect its Directors without any restriction as to their residence or citizenship, except such as may be imposed by the by-laws of said Society now in force; or as such by-laws may be amended hereafter.

SECTION 2. Said Society may hold its meetings at such times and places in this state, or elsewhere, as it may select, and all acts done without this state shall have the same force and effect as if done within this state.

SECTION 3. This act shall take effect immediately.

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### COUNCIL.

The Council has approved the election of Edward Hart as Editor for 1895.

A majority of the Council have also approved the time and place suggested for the summer meeting; *viz.*, Springfield, Mass., August 27 and 28, 1895.

#### NEW MEMBERS ELECTED APRIL 8.

Bachman, Irving A., Augusta, Ga.  
Blasdale, W. C., 2111 Channing Way, Berkeley, Cal.  
Emery, William O., Chicago Athenaeum, Chicago, Ill.  
Harding, E. P., Univ. of Minnesota, Minneapolis, Minn.  
Hooland, H. B., Univ. of Minnesota, Minneapolis, Minn.  
Lenher, V., State University, Berkeley Cal.  
O'Neill, Prof. Edmond, State University, Berkeley, Cal.  
Shepherd, R. S., Univ. of Minnesota, Minneapolis, Minn.  
Strathern, F. P., Univ. of Minnesota, Minneapolis, Minn.  
Tinsley, John D., Miller School, Crozet, Va.

ASSOCIATE ELECTED APRIL 8.

Smith, Thorn, Agricultural College, Mich.

ELECTED APRIL 9.

Davidson, G. M., 317 Linden Ave., Oak Park, Cook Co., Ill.  
Ferry, Charles, 309 2nd St., Troy, N. Y.  
Hornbeak, S. L., 578 60th St., Chicago, Ill.  
Ikuta, Massuo, Univ. of Chicago, Chicago, Ill.  
Redding, Clifford R., Chem. Lab. U. P. Ry., Omaha, Neb.  
Riggs, Prof. R. B., Trinity College, Hartford, Conn.  
Seamon, F. H., Guanacevi, Est. de Durango, Mexico.  
Smoot, Albert M., 9 Cliff St., N. Y. City.  
Wells, Horace L., Sheffield Scientific School, New Haven, Conn.

ELECTED APRIL 19.

Hall, Clarence A., 3220 Powelton Ave., Philadelphia.  
Lasher, Frederick G., 76 Newell St., Brooklyn, N. Y.  
Roegner, Edward W., 200 Jefferson Ave., Passaic, N. J.

CHANGES OF ADDRESS.

Burleigh, Wm. F., care of West Bergen Steel Works, Jersey City, N. J.  
Chase, Geo. W., 526 Quincy Ave., Scranton, Pa.  
DeChalmot, Dr. G., care of Willson Aluminum Co., Spray, Rockingham Co., N. C.  
Hand, Daniel, 62 East Park St., Newark, N. J.  
Hine, S. K., Poland, Ohio.  
Morgan, F. M., Longue Pointe, Hochilaga Co., Canada.  
Starr, H. F., 142 4th Ave., Newark, N. J.  
Waterman, C. N., Room 65, 620 Atlantic Ave., Boston, Mass.

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MEETINGS OF SECTIONS.

NEW YORK SECTION.

The regular meeting was held at the Chemical Lecture Room of the Columbia College School of Mines, on April 12, Prof. Peter T. Austen in the chair. Fifty members were present. Minutes of March meeting were omitted owing to the absence of

the Secretary, Prof. Morris Loeb. Mr. W. S. Myers was appointed secretary *pro tem.* Messrs. Richards & Co. exhibited a number of interesting forms of novel and improved apparatus including microscopes, polariscopes, aluminum ware, chemical preparations, etc. Dr. Ernest E. Smith read a paper on the Theories of the Chemical Pathology of Uraemia, describing the history and development of the various theories and giving details of experiments showing the extent of the toxic effect of urea. He held that the products of the disease are factors of varying proportions in producing the observed symptoms and effects. Prof. Charles A. Doremus, and Dr. E. R. Squibb discussed the paper. Prof. Charles F. Chandler gave a very interesting talk on Chemical Manufacture in Europe, and discussed in detail the latest processes for manufacturing sodium, aluminum, chlorine, caustic soda, coal-tar colors, and pharmaceutical preparations, which he had personally studied during a recent trip abroad. The speaker emphasized the general prosperity of the chemical industry in Germany, and also drew attention to some of the recent industrial developments in this country, in particular that of carborundum.

Dr. W. D. Horne read a paper on the "Decarbonization of Bone-Black," establishing by a number of experiments the claims for the immense saving which may be effected by decarbonizing the char in the newly patented Weinrich Apparatus. A discussion followed, in which Dr. Chandler and F. O. Mattheisen took part. Prof. Chandler asked if the amount of nitrogen in the char before and after decarbonization in the apparatus had been tested, to which Dr. Horne replied that it had not been.

Dr. Peter T. Austen explained the production of two new solid coloring matters from logwood, which he had recently patented, one of which was made by the action of ammonium carbonate upon logwood extract of high gravity, and which appeared to consist of ammonium compound of haematine, and differed from the oxidized logwood extract made by him at an earlier date by the action of sodium nitrite upon logwood extract. The other product was produced by the action of borax of high gravity logwood extract. It was stated that borax seemed to have a peculiar action on the extract of logwood,

which was not produced, so far as the speaker knew, by any other substances. The borax derivative differed from the others in not being fully oxidized, and hence contained both haemateine and haematoxylin, so that it resembled in composition the logwood extract.

The chairman stated that he was happy to announce that the society would soon be able to have quarters of its own, as two available rooms were now under consideration, and that the informal dinners would be resumed with the next meeting.

The society then adjourned.

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#### WASHINGTON SECTION.

Thursday, April 11, 1895.

President Charles E. Munroe in the chair. Fifty-three present. Dr. J. E. Blomen was elected to membership.

Mr. H. C. Sherman read a paper on "The Determination of Nitrogen in Fertilizers." Mr. Sherman stated that in determining nitric nitrogen in fertilizers containing notable quantities of chloride, the results were always too low. He obtained much better results by slightly modifying either the modified Kjeldahl or Gunning methods. In the modified Kjeldahl method Mr. Sherman recommends that the sulphuric and salicylic acid mixture be cooled before it is added to the substance under examination, and that the substance be digested in this mixture in the cold for some time before the addition of the reducing agents.

In the Gunning method Mr. Sherman obtains satisfactory results by boiling for thirty to forty minutes after the liquid has become entirely colorless.

Professor C. E. Munroe exhibited specimens of calcium carbide and discussed its value from theoretical and practical standpoints. He also generated acetylene by the decomposition of this substance with water, and showed the properties of the flame formed by its combustion. The paper was discussed by Messrs. Chatard, Clarke, and Dewey. Professor Clarke called attention to the theoretical interest of the substance. He said that calcium carbide was an interesting connecting link between organic and inorganic chemistry, the hydrogen of acetylene being

replaced by a divalent metal, and being introduced into the molecule again by the simple decomposition of water. He called attention to the fact that calcium carbide is merely an example of a series, and referred to the strontium and barium carbides of Moissan.

Mr. E. G. Runyan and Professor Wiley read a paper on "Precipitation of Small Quantities of Phosphoric Acid by Ammoniacal Citrate of Magnesium."

The principle of the method developed in the paper is based upon the observation that with quantities of phosphoric acid below five per cent., the direct citrate method gives entirely too low results. An attempt was made to remedy this source of error by adding in such cases a known volume of phosphate solution of ascertained strength in order to bring the total amount of phosphoric acid up to fifteen per cent. or more. Large numbers of analytical data were shown, illustrating the fact that by this fortification, perfectly accurate results could be obtained by the citrate method, even in samples containing a fraction of one per cent.

Professor Munroe then led in the discussion of the topic of the evening, "Can Argon be Accepted as a New Element," and reviewed the work of Rayleigh and Ramsay, Crookes and Olzewski, on this subject. Prof. Clarke stated that he had received a letter from Prof. Ramsay a few days before, asking for a sample of the uraninite in which Dr. Hillebrand reported nitrogen. Reviewing the work of Dr. Hillebrand, he said that in dissolving uraninite in sulphuric acid, he noticed that a gas was liberated steadily and uniformly throughout the whole operation. Nitric acid and ammonia were both prepared from this gas, and its spectrum was considered to be that of nitrogen, although there were some lines in the spectrum which did not belong to that of nitrogen, and were supposed to be caused by the presence of some impurity. Prof. Ramsay, in working with Cleveite, from Norway, observed a gas whose spectrum showed the more prominent argon lines, and also lines which have been ascribed to the solar element helium. The residues from Dr. Hillebrand's samples have been sent to Prof. Ramsay. Prof. Clarke said that this gas had not been found in uraninite con-

taining thorium, and suggested the possibility that the argon was combined with uranium in uraninite. Attempts would be made, he said, to combine argon with uranium.

Dr. Chatard said that it was his recollection that Dr. Hillebrand's nitrogen was very difficult to oxidize, and that the amount of oxidation products obtained was barely sufficient for their identification.

Dr. Stokes said that at Dr. Hillebrand's request, he had examined a sample of uraninite, and had not been able to detect nitrogen by the ferrocyanide reaction.

The president said that the literature of nitrogen was being reviewed, and all statements that could have any bearing on argon or which would seem to refer to argon in any way, were being noted.

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CINCINNATI SECTION.

Tuesday, April 16, 1895.

Prof. T. H. Norton, gave a very interesting account of "Recent Important Discoveries in Chemistry," dwelling particularly upon the commercial importance of calcium carbide for the production of acetylene, with a practical demonstration of the value of acetylene as an illuminant.

Papers on "Stereoisomeric Compounds of Nitrogen," by Dr. H. E. Newman, and "The Adulteration of Powdered Elm Bark," by Henry B. Foote, were postponed to next meeting.



## Proceedings.

### COUNCIL.

An invitation from Cleveland, Ohio, to hold the winter meeting at that place has been accepted by Council.

#### NEW MEMBERS ELECTED APRIL 29.

Adgate, Matthew, B.S., P. O. Box 32, Bridgeport, Conn.  
Blalock, Thomas L., B.S., 908 Canton St., Baltimore, Md.  
Dal Molin, A.A., 41 Barclay St., New York City.  
Emerson, W. H., Ph.D., Ga. School of Tech., Atlanta, Ga.  
Hinds, Prof. J. I. D., Ph.D., Cumberland University, Lebanon, Tenn.  
Koebig, Julius, Ph.D., 1824 Ellis St., San Francisco, Cal.  
Maas, Philip, 1228 West College Ave., Philadelphia, Pa.  
Miller, Dr. Stephen C., Columbian University, Washington, D. C.  
Priest, Prof. Henry, Canton, N. Y.  
Slocum, J. W., 514 Gay St., Knoxville, Tenn.

#### ELECTED MAY 16.

Keiser, Dr. E. H., Bryn Mawr, Pa.  
Ledoux, Albert R., M.S., 9, Cliff St., New York City.  
MacDowell, Wm. F., Ph.D., U. S. Immigration Service, Med. Dept., Ellis Island, N. Y.  
Porter, John Bonsall, Glendale, Ohio.  
Salisbury, Jerome H., M.D., 982 Adams St., Chicago, Ill.  
Tuthill, J. B. T., Salem Gas Light Company, Salem, Ore.  
Walker Henry V., Ph.D., 32-34 Clinton St., Brooklyn, N. Y.  
Waters, A. A., A.M., Abingdon, Ill.

#### ASSOCIATE ELECTED MAY 16.

Harris, Henry H., Ph.D., Taylor, Pa.

CHANGES OF ADDRESS.

Burrell, Loomis, Little Falls, N. Y.  
Endemann, Dr. Herman, 23 William St., New York City.  
Furgeson W. C., 40 North Parsons Ave., Flushing, N. Y.  
Graham, Wm. H., 5 Valley Place, Upper Montclair, N. J.  
Kellar, Chas., 113 Biddle Ave., Station D, Pittsburg, Pa.  
Krause, Dr. O. H., Prospect Ave., Hackensack, N. J.  
McDermot, Thomas E., Washington Ave. above 20th St.,  
Philadelphia, Pa.  
Saarback, Dr. Ludwig, 23 William St., New York City.

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MEETINGS OF THE SECTIONS.

LEHIGH VALLEY SECTION.

The regular monthly meeting was held at Lehigh University, South Bethlehem, on the evening of May 2. There were fourteen present. Porter W. Shimer read a paper on the "Determination of Graphite in Pig Iron," and Albert L. Colby followed with a talk on "The Selection of Samples for Analysis." He suggested that instruction in sampling be given to undergraduates as a regular part of their training, and that uniform methods of sampling be adopted by practical chemists.

## Proceedings.

### COUNCIL.

A committee consisting of Professors Hale, Austen and Brene-man, has been appointed by the President to consider the ques-tion of a permanent badge for the Society.

#### NEW MEMBERS ELECTED JUNE 6.

Beal, Prof. James H., Scio College, Scio, Ohio.  
Chauvenet, Wm. M., 709 Pine St., St. Louis, Mo.  
Fuller, Geo. W., Experiment Station, Lawrence, Mass.  
Gaylord, Wallace R., 146 Terrace Drive, Pasadena, Cal.  
Harrison, John B., Government Laboratory, Georgetown,  
Demerara, British Guiana.  
Hengstler, Louis, Jr., Hoboken, N. J.  
Howard, Chas. D., S.B., Newport, R. I.  
Lagai, P. G., Ph.D., 17 Park Place, New York City.  
Linebarger, C. E., South Division, High School, Chicago, Ill.  
McBryde, J. Bolton, University of Tenn., Knoxville, Tenn.  
McClure, Prof. Edgar, University of Oregon, Eugene, Ore.  
Pagelson, Otto H., 2421 Dearborn St., Chicago, Ill.  
Peacock, Samuel, 47 South 17th St., Philadelphia, Pa.  
Rich, H. L., Lasell Seminary, Auburndale, Mass.  
Richardson, Geo. M., Stanford University Cal.  
Wellington, Harry T., Wellington Manufacturing Co., 468  
and 470 Cherry St., New York City.

#### CHANGES OF ADDRESS.

Barba, W. P., 5110 Newhall St., Germantown, Phila., Pa.  
Brown, Lucius P., 150 North Cherry St., Nashville, Tenn.  
Behr, Arno, 171 Grand Ave., Pasadena, Cal.  
Benton, Geo. W., High School, Indianapolis, Ind.  
Bird, Herbert S., care of N. Y. Tartar, Co., 9th St. and  
Gowanus Canal, Brooklyn, N. Y.  
Cambier, Jacob, 1000 Abriendo Ave., Pueblo, Colo.  
Carpenter, Thos. B., 325 Jersey St., Buffalo, N. Y.  
Chase, Geo. W., Thomas, Ala.  
Clapp, Geo. H., 325 Water St., Pittsburg, Pa.  
Collins, W. H., 6757 Perry Ave., Chicago, Ill.  
Clymer, Edwin S., 45-47 Reed St., Reading, Pa.

- Doolittle, O. S., 130 North 5th St., Reading, Pa.  
Evans, Thomas, Chemist American Cotton Oil Co., 46 Cedar St., New York City.  
Feid, George F., 199 Findlay St., Cincinnati, Ohio.  
Hochstetter, Robert W., Oak and Bellevue Sts., Mt. Auburn, Cincinnati, Ohio.  
Linn, A. F., Park Place, Springfield, Ohio.  
Lustig, A. L., P. O. Box 582, Providence, R. I.  
Maxwell, Dr. Walter, Sugar Experiment Station, Honolulu, S. I.  
Nichols, Wm. H., 47 Cedar St., New York City.  
Pearce, Edward D., care of L. P. Shepard and Co., Providence, R. I.  
Powell, J. W. Bureau of Ethnology, Washington, D. C.  
Rosengarten, Geo. D., 1700 Fitzwater St., Philadelphia, Pa.  
Schimpf, Henry W., 365 Franklin Ave., Brooklyn, N. Y.  
Simonson, W., 901 Race St., Cincinnati, Ohio.  
Smith, Thorn, Agricultural College, Lansing, Mich.  
Stone, W. G., 302 Union St., Brooklyn, N. Y.  
Taylor, Thomas, M.D., 238 Massachusetts Ave., N. E., Washington, D. C.  
Waller, Elwyn, 440 First Ave., New York City.  
Wesson, David, University Heights, N. Y.  
Wickhorst, Max H., 268 Forquer St., Chicago, Ill.  
Wood, E. F., Munhall, Pa.  
Wood, Edward S., 688 Boylston St., Boston, Mass.  
Wulf, Henry C., care of Pacific Mill Co., San Francisco, Cal.  
Youmans, W. J., 72 Fifth Ave., New York City.

## MEETINGS OF THE SECTIONS.

### RHODE ISLAND SECTION.

The March meeting was held Thursday evening, March 21. J. P. Famworth, Esq., read a paper on the "Selection of Water for Bleaching and Other Manufacturing Purposes."

The April meeting was held Thursday evening, April 23. Mr. H. S. Bingen presented a paper entitled "A Resumé of the Methods of Bleaching Cotton Piece Goods."

The May meeting was held Thursday, May 23. Edward D. Pearce, Esq., presented a paper on "Pollen." The paper contained suggestions as to the nature of the color of pollen grains, with a review of methods of mounting, and the effect upon the coloring-matter of various mounting media. The paper was

illustrated by twenty-five typical slides exhibited under the microscope.

The June meeting was held Thursday, June 13th, 12 m. This being also the Annual meeting, the first business was the election of officers for the ensuing year, which resulted as follows: Presiding Officer, Mr. Charles A. Catlin; Secretary and Treasurer, Prof. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

After the transaction of other business relating to the work of the Section for the coming year, the Chairman presented his annual address, taking as his topic, "Chemical Laboratory Microscopy," advocating a more thorough training of young chemists in microscopy, specially and directly applied to chemical laboratory work. Presenting and discussing recent advances in micro-physiography, crypto-chemistry, and micro-chemical reactions, he described and illustrated some original methods and apparatus of his own, more particularly a method of mounting for the purpose of localizing the individual particles in samples of powdered material, by means of adhesive films upon slides having engraved or etched numbered squares, thus fixing each in certain definite portions for purpose of subsequent identification through optical behavior, physical form, or reaction with reagents. He further suggested and illustrated the valuable service that may be obtained from cultures of some of the lower organisms in the classification of turbid solutions, more especially, the removal of suspended finely divided carbon, such as at times results from the carbonizing of organic matter in the presence of fluxing and other salts, the suspended matter of such solutions being attracted and entangled in the mycelium of the fungus growth induced therein, and thus with it easily removed. He finally discussed micro-chemical reactions in their bearing upon qualitative chemical analysis, urging a more complete classification of the facts relating to reactions already studied, with the view of elaborating a less complicated scheme of micro-chemical analysis than any suggested, commending the works of Klément and Rénard, of Haushofer and of Behrens, as worthy of confidence. In his own work he found the greatest usefulness of micro-chemical analysis, not in any scheme, but as auxiliary

to the ordinary course of qualitative analysis, through special reactions curtailing oftentimes to a remarkable degree its tedious separations, and further, finding in it an approximate qualitative value far exceeding the indications of ordinary qualitative work in this direction; and suggested possibly the attainment of very close approximations quickly, by comparison of reactions with standards of known value.

During an intermission, the members in attendance enjoyed a delightful lunch in one of the private dining rooms of the famous Hope Club.

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CINCINNATI SECTION.

The meeting was held Wednesday, May 15, Dr. Alfred Springer presiding.

Mr. Henry B. Foote read a paper on "The Adulteration of Powdered Elm Bark." He stated that in his opinion the microscope was the only reliable means of detecting adulterations in the powdered bark. He thought no reliance should be placed on the starch test, as the liber of young trees contained starch but no reaction could be obtained from bark from old trees.

Prof. T. H. Norton read a paper on "Ammonium Thioacetate." After speaking of the many advantages of this over hydrogen sulphide as a precipitant, he demonstrated practically the ease with which the arsenites and arsenates could be completely precipitated from solution.

Adjourned until October 15.

## Proceedings.

### CHANGES OF ADDRESS.

Dorr, John V. U., care of D. & D. Smelting Co., Deadwood, S. D.

Emery, Sidney S., care of Repauno Chem. Co., Chester, Pa.

Girling, R. N., 2728 Prytania St., New Orleans, La.

Howard, C. D., Durham, N. H.

Howe, Fred. W., 53 Monument Ave., Charlestown, Mass.

Kenan, Wm. R., Jr., Univ. of N. C., Chapel Hill, N. C.

Lammers, Theo. L., 32 Pittsburg Block, Helena, Mont.

Neiman, Howard S., 8 East 97th St., New York City.

Newman, H. E., 261 Central Ave., Cincinnati, O.

Seamon, W. H., School of Mines, Socorro, New Mexico.

Starke, Frederick W., 4169 Leidy Ave., West Philadelphia, Pa.

Wardman, Geo. B., care of La Gran Fundicion, Central Mexicana, Agnos Calientes, Mexico.

White, Annie E., 71 Forest Ave., Buffalo, N. Y.

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### MEETINGS OF THE SECTIONS.

#### CHICAGO SECTION.

At a meeting held June 3, in the chemical lecture room at the Northwestern University, School of Pharmacy, the Chicago Section of the American Chemical Society was organized with the following officers: Frank Julian, President; J. C. Foye, Vice-President; F. B. Dains, Secretary; J. H. Long, Treasurer. Executive Committee, Frank Julian, A. L. Smith, and F. B. Dains.

The Section then adjourned until the regular meeting in September.





## Proceedings.

### ELEVENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

#### MINUTES.

The Eleventh General Meeting of the American Chemical Society was held in Springfield, Mass., August 27 and 28, 1895.

The meeting was called to order in Evangelist Hall, at 10 A. M., August 27, by the President, Professor Edgar F. Smith of Philadelphia.

President Smith introduced Mayor Charles L. Long, of Springfield, who spoke a few words of welcome to the Society, as follows:

"Mr. President and Members of the American Chemical Society. I cannot claim that the words I shall speak to you will rise to the dignity of an address. It was suggested to me that I should welcome the Society to Springfield, and this I most cordially do.

This is an occasion of great interest to our people. Nothing like it has occurred since the meeting of the American Association for the Advancement of Science here in 1859. You have met as the representatives of a great branch of science.

If I were called upon to name that branch of science that has accomplished the most practical results for mankind, I should say chemistry. The debt of gratitude that humanity owes to chemistry can never be repaid. Look at the results it has secured. Take for example, the Chemistry of Agriculture, it has made the earth to yield bountiful harvests. Then, too, the matter of foods and the preparation of foods for human consumption. Chemistry has given to the world the means for detecting the adulteration of foods. There is hardly an article that forms the dress of man or woman that does not owe its value to the skill of the chemist. In medicine, chemistry has done great service to man in providing cures for the various ills of the human body. For this mankind cannot be too grateful.

When the sun has set beyond the western hills and darkness has come on, you will find that the chemist has turned night into daylight in giving us the products of petroleum and illuminating gas, whether obtained from the destructive distillation of coal, or by the decomposition of steam. And so throughout the realm of human wants.

Why, then, should I not welcome to the city of Springfield, the representatives of a branch of science to which mankind is indebted more than to any other of the various branches of science? I trust your stay will be pleasant and that your deliberations will be profitable, and that after partaking of the hospitalities here, you will safely return to your respective homes."

President Smith, in behalf of the Society, replied:

"Mr. Mayor: In response to your very cordial invitation to come and take possession of the land, as it were, permit me to return the hearty thanks of the Society. We anticipate much pleasure and profit in our visit to this progressive city, known throughout the land as the place where so many scientific appliances are utilized. We shall gladly avail ourselves of the opportunities you offer.

In bidding us welcome to your city, you introduce to your fellow citizens the representatives of the youngest national chemical society, national in that its representatives are found in the east, the west, the north and the south. In recent years, also, the names of prominent European chemists have appeared upon our roll. Our object is to bring together all who cultivate the science of chemistry. In our membership of about one thousand, there are found many engaged in agriculture, in botany, in the iron industry, in coloring, and last but not least, the ubiquitous teacher of chemistry.

This Society fosters research, research not only in one direction, but in all. We have chemists interested in every department of chemistry. In this respect the American Chemical Society is unique, it stands alone. The great object of this Society is to make the science of chemistry in every way helpful to our fellow men.

Permit me, in advance, to thank you for the many hospitalities of which we shall be the recipients. We have nothing to offer in return unless you shall feel inclined to remain with us and listen to our papers and discussions."

At the conclusion of these remarks the President announced that the Society was ready for the presentation of papers and called upon Dr. W. A. Noyes, who read a paper on the "Determination of the Heating Effects of Coal," prepared by himself in conjunction with J. R. McTaggart and H. W. Craven. Dr. Noyes' paper was discussed by Drs. Hart and Prescott, after which Prof. F. P. Venable presented a paper entitled "A Case of Mistaken Identity." There was a short discussion on the paper by Drs. Hart and Prescott and President Smith, followed by a few remarks by the author.

The next paper was upon "The Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere," by Prof. Francis C. Phillips. This was discussed by Drs. W. A. Noyes, Edward Hart and E. E. Smith. Then R. P. Williams presented a paper on "A new Electrical Process for Making White Lead," which was discussed by Messrs. Meyers, Prescott, Hart, E. F. Smith and T. H. Norton.

Dr. A. A. Noyes read a paper on "The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solutions," and this was followed by another paper by the same author on "The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture." There were some discussions and questions on the last paper by Messrs. W. A. Noyes and A. B. Prescott, and a brief reply by the author.

An informal report of the present condition of the Society was given by the General Secretary, who announced the establishment of two local sections since the last meeting, one in Nebraska, with headquarters at Lincoln, Nebr., and the other in the city of Chicago. The membership of the Society was stated to be just 900. There are also some persons who have been elected but have not yet qualified, and quite a number of persons whose applications for membership have been favorably reported by the Standing Committee on Nominations to membership, so that practically the number of members may be considered as about 950.

The following named members have died since the report given at the last General Meeting:

Dr. A. A. Fesquet, Dec. 26, 1894.  
 Prof. H. B. Nason, Jan. 17, 1895.  
 J. C. Dittrich, (drowned on the Elbe) Jan. 1895.  
 W. H. Whalen, Feb. 3, 1895.  
 Prof. Mark Powers, Mar. 1, 1895.  
 Lewis Hoffman, Mar. 4, 1895.  
 Dr. Gideon E. Moore, April 15, 1895.  
 W. G. Wallace, April, 1895.  
 Wm. C. Wilson, April 16, 1895.

There are now eight Local Sections of the Society; *viz.*, Rhode Island, Cincinnati, New York, Washington, Lehigh Valley, New Orleans, Nebraska and Chicago.

A bill was passed by the legislature of the State of New York during its last session, allowing the Society to elect its directors without regard to their residence or citizenship, and legalizing all action of the Society that may be taken at any of its meetings outside of the State of New York. Prof. F. W. Clarke, chairman of the committee appointed to consider the question of amendments to the constitution, has resigned, and Dr. H. W. Wiley has been appointed to fill the vacancy.

After the report by the General Secretary and certain announcements regarding excursions, visits, and sessions of the Society, a paper on "The Determination of Sulphur in Refined Copper," by George L. Heath, was read by Dr. Wm. McMurtrie, the author being absent. The morning session was then adjourned.

In the afternoon the chemists made an excursion to Holyoke, leaving Springfield at 1 P. M. and returning in time for the evening session. At Holyoke they visited the mills of the Holyoke Paper Company, the Merrick Thread Company, and the Farr Alpaca Company.

At 1 P. M. under the guidance of Messrs. H. H. Bosworth, C. M. Kirkham, J. Eastman Belding and H. S. Anderson of the Local Committee, the chemists took the electric car for Holyoke. They visited first the mills of the Holyoke Paper Company. Mr. Oscar Greenleaf, Treasurer of the Company, conducted the party through the building and explained to them very clearly and minutely the various steps in the manufacture of paper from the beginning to the end.

The company use both American and foreign rags. The rags are first dusted in a star-shaped holder, which, by its revolution, allows the rags to fall down from one star-point to another thus driving out the dust which escapes through the meshes of the sieve-like sides of the holder.

After being dusted the rags are placed upon tables where they are picked over by hand, and buttons, hooks and eyes, pieces of whalebone, rubber, etc., are removed, scythes being used to cut them off when possible. Sometimes valuable articles are found and these the workers are allowed to keep. This furnishes a valuable incentive for the careful examination of the rags. After the first picking-over the rags are examined again by another person and any remaining objectionable articles removed, and the rags are also sorted into different grades. The rags are then passed between closely fitting cogs which tear them into shreds,

after which they are chopped into small pieces by an instrument in which the knives revolve in a manner similar to those of a lawn mower. After this the rags are sometimes subjected to another process of dusting by being whipped while in a suitable receptacle.

They are then put into large revolving cylinders and boiled under pressure of thirty-five to fifty pounds in milk of lime of about the consistency of cream. After being thus treated sufficiently they are removed, the lime allowed to drain off, and the rags are then put into washing engines, where they are reduced to pulp, a stream of clear spring water flowing in and a stream of dirty water flowing out continuously at the other end of the washing machine.

The rags are reduced to pulp by the scraping action of steel bars, those of one set passing through the narrow spaces between the others and thus drawing out the fiber somewhat like the process of scraping cloth for lint. When the rags have been reduced to pulp and sufficiently washed, a solution of chloride of lime is run in for the purpose of bleaching the pulp. At this stage the flow of water in and out of the vat is checked, as is also the pulp-reducing action of the machine, and the mechanical action is simply such as to keep the bleaching pulp stirred and rotating around in the vat of the machine.

After being bleached the pulp is allowed to flow into draining rooms, *i. e.*, into large receptacles containing a perforated bottom, where it remains from five days to three or four weeks, according to the requirements. The chloride-of-lime water is there drained off.

The bleached and drained pulp is then put into beating engines, where it is washed with water to remove any remaining chloride of lime, and if necessary, sodium hyposulphite is added to neutralize the last traces of the chloride. It is here reduced to a very fine fiber. Then it is put into a large tank and pumped on to a paper machine having a large endless piece of wire cloth, which is drawn along and carries with it the fiber thinned with a sufficient amount of water. In this operation the cloth is given a shaking motion, and as the water runs off the fibers are shaken closely together, interlaced more or less, and packed down so as to cohere into one continuous sheet. The remaining water, so far as possible, is withdrawn from the fiber by a suction pump.

From the wire cloth the paper passes between heavy rollers and upon a sheet of woollen felt. Thence it goes over iron cylinders heated inside with steam. After the paper is thus dried, it is passed through a solution of glue or extract of rawhide. This animal sizing is thus absorbed by the paper, some vegetable sizing having been already introduced into the material in the beating engine. The vegetable sizing is resin. The paper, wet with animal sizing, is hung over poles where it dries slowly. If rapidly dried, the strength of the glue is partly destroyed.

When dried, the paper is calendered. There are two methods of calendering: (1) the American, by which the paper passes between rolls,

three of chilled iron and two of paper arranged alternately ; (2) the foreign, by which the paper is pressed between two heavy chilled rolls after having been packed in layers between zinc or pasteboard plates.

The best quality of paper is not weighted. No weighting is done at the mills of the Holyoke Paper-Co. Whenever weighting is done at all, the weighting—or filling—material is introduced into the heating engines with the pulp.

Mr. O. S. Greenleaf, Treasurer of the Holyoke Paper Co., in addition to his other many courtesies, sent to the General Secretary a package containing a sample box of paper and envelopes for each of the chemists who had visited their mill. These were not received until after the adjournment of the meeting and some of the chemists had left the city, but the boxes were distributed to all who were still accessible and the General Secretary, in behalf of the members, sent a letter to Mr. Greenleaf, expressing their cordial thanks for this pleasing souvenir of their visit.

The evening session on Tuesday, Aug. 27, was held in room 6 of the High School, President E. F. Smith presiding. A paper upon "The Speed of Oxidation by Chloric Acid," prepared by Dr. R. B. Warder and Herman Schlundt, was read by Dr. Warder and afterwards discussed by Drs. Norton, A. A. Noyes and Warder. This was followed by a paper on "The Reaction between Copper and Concentrated Sulphuric Acid," by Chas. Baskerville. The subject of Mr. Baskerville's paper was discussed by Dr. Andrews, after which a few words of reply were offered by the author.

The closing paper of the evening session was read by Prof. Francis C. Phillips. The subject of the paper was, "The Evolution Method for the Determination of Sulphur in Iron." After the reading of the paper the subject was discussed by Dr. Hart, and then after some announcements by the Secretary, the evening session was adjourned.

The Society assembled for its morning session Aug. 28, at 9 A. M. in Evangelist Hall, President Smith in the chair. Dr. Norton read a paper upon "The Use of Aluminum for Condensers," and this was discussed by Drs. Hale, McMurtrie and others. A paper upon "Arsenic in Glycerol," prepared by Geo. E. Barton, was read by Dr. McMurtrie in the absence of the author. The subject was discussed by Messrs. Prescott, W. P.

Mason and Munsell. Then followed a paper presented by Mr. Lyman F. Kebler on "The Acidimetric Estimation of Vegetable Alkaloids." This paper elicited considerable discussion, the following named gentlemen taking part: Messrs. Prescott, W. A. Noyes, Sabin, W. P. Mason, Bigelow, Munsell, Andrews and Kebler.

The next paper was upon "Metaphosphinic Acids and their Derivatives," by Henry N. Stokes, and a few remarks were made upon this paper by Dr Norton. Chas. H. Herty then presented a paper on "Observations on Double Platinum Salts." This was discussed by Messrs. Stokes, Howe, W. P. Mason and Myers, after which Dr. Launcelot W. Andrews read a paper on "The Analysis of Alloys containing Tin, Lead and Antimony.

After the General Secretary had made some announcements, Wm. K. Robbins described a new burette holder, designed by himself, and Dr. A. A. Noyes announced the publication of the "Review of American Chemical Research," and distributed specimen pages of the periodical to the members present. Prof. W. P. Mason described a new kind of water-bath. Dr. Hart, in the absence of the author, read a paper upon "Tellurium, its Separation from Copper Residues, with Notes on some New Reactions," prepared by Cabell Whitehead.

President Smith then invited Prof. E. W. Morley, President of the American Association for the Advancement of Science, to address the Society. Dr. Morley in reply made some informal remarks, summing up the results of investigations that have been made upon the "Atomic Weight of Oxygen," which, by any reasonable system of averaging the results of all of the most reliable investigations, was shown to be 15.879. President Smith thanked Prof. Morley very heartily for his remarks, and in most complimentary terms showed how the chemists of America are to be congratulated upon having among their number, one whose own research upon the atomic weight of oxygen would rank among the most profound and reliable investigations that have ever been made upon that subject by any scientist of any country.

Dr. A. B. Prescott said, "I can add nothing to the words

already spoken in congratulation to this Society and to this meeting, words most fit to be spoken at this time, in all of which I desire most sincerely to join. If I would add another word to express what has been in my heart as we sat here, it would be a word of acknowledgment for us all, of what we owe to our presiding officer in this meeting. He has conducted our discussions with equal interest and spirit in all subjects, suggesting fruitful inquiry and saving the valuable time of the meeting, crowded as it has been with papers and living topics. I am sure I can speak for every member of the Society in giving thanks to both the General Secretary and the President for their tireless and effective service in preparing for this meeting and conducting it throughout."

Drs. Hart and Norton followed briefly with similar remarks, and upon motion of Dr. Hart, the Society passed a vote of thanks to the President and General Secretary in harmony with the sentiments that had just been expressed.

Upon motion of the General Secretary the thanks of the Society were extended to the Local Committee of Arrangements in Springfield for their untiring efforts to make the meeting of the chemists a pleasant and successful one, and especially to the Local Secretary, Mr. Wm. A. Webster. Also to Prof. Wm. Orr, Jr., Chairman, and Mr. Henry H. Bosworth, Secretary of the Committee on Excursions; to Mr. C. M. Kirkham, Mr. J. Eastman Belding, and Mr. H. S. Anderson; to the officers of the Holyoke Paper Company for permission to visit their mills and to Mr. O. S. Greenleaf, Treasurer of said Company, and Mr. C. J. Humes-ton; to the Farr Alpaca Company, and especially to Mr. H. M. Farr, Agent, and Mr. F. H. Metcalf, Superintendent; to the Merrick Thread Company, and especially to Mr. O. H. Merrick, Superintendent, and Mr. S. M. Bentley; to the United Electric Light Company, the Hampden Paint and Chemical Company, and to the officers in charge of the United States Armory, especially to Col. Alfred Mordecai, Major W. H. Rexford and Lieut. Tracy C. Dickson, for their personal and official courtesies; to the hotels and railroad companies for reduced rates; to the local press for their careful and complete reports of the meeting, and to the citizens of Springfield generally for their many



hospitalities and their efforts to make our visit to their city pleasant and our meeting successful.

The remaining visits to be made by the chemists were announced, after which the Eleventh General Meeting of the Society was formally adjourned.

According to the announcements made the members visited the United States Armory and the Hampden Paint and Chemical Works during the afternoon, and early the following morning those who cared to go were very courteously received at the plant of the United Electric Light Company by Mr. H. S. Anderson, electrician, who conducted them through the works and showed them many very interesting experiments with high tension currents. This formed a very fitting termination of one of the most enjoyable and successful meetings the Society has ever held.

The following members registered in attendance at the meeting:

Edgar F. Smith, Philadelphia, Pa.  
 Albert C. Hale, Brooklyn, N. Y.  
 Wm. McMurtrie, Brooklyn, N. Y.  
 Edward Hart, Easton, Pa.  
 Wm. Bromwell, Port Deposit, Md.  
 W. D. Bigelow, Washington, D. C.  
 A. H. Sabin, New York.  
 Wm. Frear, State College, Penna.  
 Francis C. Phillips, Western Univ., Allegheny, Pa.  
 Rufus P. Williams, English High School, Boston.  
 Robt. B. Warder, Washington, D. C.  
 Frank N. Guild, Greensboro, Vt.  
 A. F. Linn, Wittenberg College, Springfield, O.  
 Fred. W. Morse, N. H. Expt. Sta., Durham, N. H.  
 Arthur A. Noyes, Mass. Inst. of Tech., Boston, Mass.  
 J. A. Deghuee, Brooklyn, N. Y.  
 W. A. Noyes, Terre Haute, Ind.  
 Mary Engle Pennington, Philadelphia, Penna.  
 Elizabeth A. Atkinson, Three Tuns, Penna.  
 E. W. Allen, Washington, D. C.  
 Alfred H. Mason, New York.  
 J. B. Lindsey, Amherst, Mass.  
 A. B. Prescott, Ann Arbor, Mich.  
 F. P. Venable, Chapel Hill, N. C.  
 Ernest Ellsworth Smith, New York.

Frank D. Maine, Springfield, Mass.  
Otis C. Johnson, Ann Arbor, Mich.  
Thomas H. Norton, Cincinnati, O.  
Chas. Baskerville, Chapel Hill, N. C.  
J. Bird Moyer, Univ. of Penna., Philadelphia.  
C. Smith Boynton, Burlington, Vt.  
B. B. Ross, Auburn, Ala.  
B. W. Kilgore, Raleigh, N. C.  
Francis E. Bates, Westfield, —.  
John A. Myers, Morgantown, W. Va.  
Charles L. Parsons, Durham, N. H.  
William P. Mason, Troy, N. Y.  
Alfred Springer, Cincinnati, O.  
Launcelot Andrews, Iowa City, Ia.  
Lyman B. Hall, Haverford, Pa.  
L. P. Strong, Springfield, Mass.  
Leslie A. Cooper, Springfield, Mass.  
Wm. Woodhouse, North Adams, Mass.  
P. H. Rolfe, Lake City, Fla.  
F. Atwood Sirrine, Jamaica (L. I.) N. Y.  
Geo. W. DeWolf, Springfield, —.  
Chas. H. Herty, Athens, Ga.  
Lyman F. Kebler, Philadelphia, Pa.  
Charles E. Munsell, Brooklyn, N. Y.  
T. R. White, New York.  
George D. Gable, Fairfield, Iowa.  
Jas. Lewis Howe, Washington and Lee Univ., Lexington, Va.  
W. K. Robbins, Manchester, N. H.  
H. N. Stokes, Washington, D. C.  
Walter E. Smith, Providence, R. I.  
W. O. Atwater, Middletown, Conn.  
Charles E. Munroe, Washington, D. C.  
Edward W. Morley, Cleveland, Ohio.  
Mrs. E. F. Smith, Philadelphia, Pa.  
E. D. Campbell, Ann Arbor, Mich.  
Mary F. Leach, Mt. Holyoke College, S. Hadley, Mass.  
Paul C. Freer, Ann Arbor, Mich.  
Clara A. Pease, High School, Hartford, Conn.  
Frank E. Coombs, Natick, Mass.  
E. Twitchell, Cincinnati, O.

ALBERT C. HALE,  
General Secretary.

## NEW MEMBERS ELECTED SEPT. 21.

Ando, Shinichi, care of Apollo Iron and Steel Co., Apollo, Pa.  
 Carnell, Wm. C., lab. Ill. Steel Co., So. Chicago, Ill.  
 Crane, Wm. H., M.D., 92 W. 7th St., Cincinnati, O.  
 DeFremery, J. L., 44 Broadway, N. Y. City.  
 DeRoode, Rudolf, care of Fraser & Co., 262 5th Ave., N. Y. City.  
 DuPont, Francis G., Wilmington, Del.  
 Johnson, Jesse F., care of Hamilton Powder Co., Montreal, Can.  
 Macadam, Wm. Ivison, Surgeon's Hall, Edinburgh, Scotland.  
 Swett, Charles E., 23 Bolander St., Providence, R. I.  
 Thackray, George E., Cambria Iron Co., Johnstown, Pa.

## ASSOCIATE ELECTED SEPT. 21.

Read, Frederick, 140 Nassau St., N. Y. City.

## CHANGES OF ADDRESS.

Allen, W. N., 2 Chestnut St., Philadelphia, Pa.  
 Barton, G. E., Columbian Univ., Washington, D. C.  
 Brinker, Harry L., 811 West Federal St., Youngstown, O.  
 Chase, George W., Bellwood, Pa.  
 Dewey, F. P., 702 Ninth St., N. W., Washington, D. C.  
 Fuller, Fred D., 7 Dix St., Worcester, Mass.  
 Gudemann, Edw., Davenport, Iowa.  
 Hand, Daniel, Edison Lamp Works, Harrison, N. J.  
 Hershey, A. N., care of A. L. Thomsen, Mfg. Chemist, Baltimore, Md.  
 Hoffman, Philip C., care of Georgia Chemical Works, Augusta, Ga.  
 Innes, Murray, care of Old Dominion Copper Co., Globe, Arizona.  
 Lammers, Theodore L., Townsend, Montana.  
 Leighton, Virgil L., Tufts College, Mass.  
 Linebarger, C. E., 2601 Calumet Ave., Chicago, Ill.  
 Loeb, Dr. Morris, 112 N. 72d St., New York City.  
 Meeker, G. H., care of Andover Iron Co., Phillipsburg, N. J.  
 Mellen, E. D., 9A Forest St., N. Cambridge, Mass.  
 Peacock, S., care of Nolan Pub. Co., P. O. Box 2113, Philadelphia, Pa.  
 Pemberton, H., Jr., 2027 Spruce St., Philadelphia, Pa.  
 Puckner, W. A., 73 Wells St., Chicago, Ill.  
 Seamon, F. H., Apartado 101, Matehuala Est San Luis Potosi, Mexico.  
 Seher, August, 115 Chestnut St., Newark, N. J.  
 Trimble, Henry, 145 N. 10th St., Philadelphia, Pa.  
 Wesson, David, The Wesson-Nivison Mfg. Co., Cortlandt, N. Y.

## MEETINGS OF THE SECTIONS.

### RHODE ISLAND SECTION.

The first meeting of the new year, 1895-96, was held at Providence, Thursday evening, Sept. 26, 1895. Prof. J. H. Appleton, of Brown University, gave an address on "Sugar and Sugar Refining," illustrated by about sixty slides shown by the lantern. Many of the slides were from negatives taken in remote sugar-producing countries, *e. g.*, Sandwich Islands, South Africa, and of course, Cuba.

## Proceedings.

### NEW MEMBERS ELECTED OCT. 10.

Browne, Arthur Benjamin, 119 Water St., Boston, Mass.  
Burt, M. C., Amherst, Mass.  
Chamberlain, Geo. D., care of Iroquois Furnace, S. Chicago, Ill.  
Johnson, Edward S., Park Bros. & Co. Steel Works, 33d and  
Smallman Sts., Pittsburgh, Pa.  
Lindsey, J. B., Ph.D., Expt. Station, Amherst, Mass.  
Louderbeck, Harry C., Griffin Wheel Co., Chicago, Ill.  
Lovejoy, Ellis, Union Furnace, Ohio.  
McCrae, John, Ph.D., Univ. of Cincinnati, Cincinnati, Ohio.  
Noyes, Dr. Arthur A., Mass. Inst. of Tech., Boston, Mass.  
Sanborn, E. R., Sharon, Pa.  
Taylor, Edward R., S. B., Cleveland, Ohio.  
Underwood, Edward L., Canton, Mass.  
Wakeman, Alfred J., 819 Madison Ave., N. Y. City.  
Withers, W. A., Raleigh, N. C.

### CHANGES OF ADDRESS.

Couch, Guy E., Pottsville, Pa.  
Drown, Thomas M., South Bethlehem, Pa.  
Fuller, Geo. W., Box 614, Louisville, Ky.  
Hornbeck, S. L., Tehuacana, Texas.  
Linn, Prof. A. F., Wittenberg College, Springfield, O.  
Moale, Philip R., care of N. Y. and Boston Dyewood Co., Green  
and West Sts., Greenpoint, Brooklyn, N. Y.  
Nicholson, Edward E., 716 University Ave., S. E., Minneapolis,  
Minn.  
Pearce, Edward D., care of T. P. Shepard & Co., Box 1336,  
Providence, R. I.  
Sherman, H. C., 252 W. 53d St., New York City.

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## MEETINGS OF THE SECTIONS.

### LEHIGH VALLEY SECTION.

The Fall meeting of the Lehigh Valley Section was held at Bethlehem, October 10. Thos. Tyrer, President of the Society of Chemical Industry of England, was the guest of the Section,

and he was accompanied from New York by representatives of the New York Section of the Society of Chemical Industry and the New York Section of the American Chemical Society, in a parlor car, kindly provided by the Lehigh Valley Railroad. It had been hoped that Ludwig Mond, F. R. S., who accompanied Mr. Tyrer to America, would also be present, but he was prevented by business engagements.

Reaching Bethlehem at 10.30 A. M., the party inspected the works of the Bethlehem Iron Co., and the officials took them through every department of the government plant. After visiting the laboratory, which through the labors of Albert L. Colby, formerly chemist, now metallurgical engineer, and C. A. Buck, chief chemist, is probably the best equipped in its facilities for doing rapid work of any in the country. The company provided their guests with a dinner served in the works offices, to which forty-two sat down.

The stated meeting was held at 4.30 P. M., Prof. Edward Hart, presiding officer in the chair.

Albert L. Colby read a paper on the "Rapid Methods perfected in the Laboratory of the Bethlehem Iron Co., and in Use There." At the close, he presented each member with a novel souvenir, a nickel-plated armorplate washer manufactured by the company, on which was stamped the date and place of meeting of the Section and the name of the person to whom it was presented. In the centre was engraved, "Accurately analyzed for carbon in 12 minutes, Manganese in 10 minutes, Phosphorus and Silicon in 30 minutes."

Other papers were read as follows: "Chemical vs. Bacteriological Examination of Water." Prof. Wm. P. Mason, of Troy, read by Dr. Wm. McMurtrie. "On Standardization of Iodine Solution," by G. H. Meeker. "A Device for Sampling Metals," by Porter W. Shimer."

Following the reading of papers, interesting responses were made by Thos. Tyrer, Esq., Alfred Mason, and Peter T. Austen. The New York delegation made the return trip at 6.30 P. M., and the meeting was voted to be the most successful one in the history of the Section.

ALBERT H. WELLES, Secretary.

## CINCINNATI SECTION.

A meeting of the Cincinnati Section was held on October 15.

Dr. Alfred Springer presented "A Tribute to Pasteur," and papers were read on "The Laboratory Uses of Aluminum" and "Recent Progress in Theoretical Chemistry" by Prof. T. H. Norton.

Dr. John McCrae, instructor in chemistry, University of Cincinnati, and Prof. A. F. Linn, professor of chemistry, Wittenberg College, Springfield, O., were elected members of the Section.

## RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence on Thursday evening, Oct. 17, 1895, Chairman C. A. Catlin, presiding.

Dr. H. J. Wheeler, of the Rhode Island Agricultural Experiment Station, read a paper upon "Acidity of Soils and its Relation to the Growth of Agricultural Plants and to the Development of the Potato Scab."

Attention was called to the fact that though the mention of sour soils appears to be almost universal, it is but rarely that any writer on agricultural chemistry has called attention to the fact that upland, light, and naturally well-drained soils are ever so acid as to be injurious to the growth of plants, and then generally, only where acidity was concluded. Instances of the occurrence of a degree of acidity in soils of this character sufficient to be injurious to many agricultural plants were cited from places in Massachusetts, Maryland, and Kingston, West Kingston, Westerly and Hope Valley, R. I. Acidity apparently of an equal degree, has been observed in many other places in New England where the effect of the same has not yet been established by actual experiments. In the course of the experiments at the R. I. Agricultural Experiment Station, covering a period of three years, over ninety varieties of plants have already been employed. The most marked differences in the effect of acid soils before and after liming have been observed in connection with plants which have ordinarily been grouped as requiring similar soil and fertilization. Photographs were shown illustrating that the presence of carbonates or the existence of acidity in soils has a wonderful

(66)

effect upon the development on potato tubers of the bacterioid fungus which causes the potato scab. The necessity for acid tests in soils of the above-mentioned character, particularly when derived from certain granites and mica schists, was strongly emphasized.



## Proceedings.

### COUNCIL.

The following have been approved by the Council :

*By-Law.*—If any member who is already a Councilor or Director shall be elected to an office which makes him *ex-officio* a Councilor or Director, the acceptance of such office shall be considered to involve the resignation of his former position as Councilor or Director, and the position so vacated shall be filled in the manner prescribed by the constitution.

*Resolution.*—Ordered that the dues for membership for 1896 be collected by the General Secretary as in the current year, and that he be allowed 10 per cent. on all collections as compensation for his work.

Cleveland has been designated as the place for the coming annual meeting, to be held on Monday and Tuesday, December 30 and 31, 1895.

The bill of the Chemical Publishing Co. for \$256.95, for the October number of the Journal, has been approved.

#### NEW MEMBERS ELECTED NOVEMBER 2, 1895.

Asbury, S. E., West Raleigh, N. C.

Atkinson, Miss Elizabeth A., 125 W. Tulpehocken St., Germantown, Philadelphia, Pa.

Best, Otto, Ph.D., care N. Y. Tartar Co., 9th St. and Gowanus Canal, Brooklyn, N. Y.

Bizzell, J. A., West Raleigh, N. C.

Conklin, E. S., care S. S. White Dental Mfg. Co., Prince's Bay, Staten Island, N. Y.

Dow, Allan Wade, District Building, Washington, D. C.

Hall, Clarence A., 3220 Powelton Ave., Philadelphia, Pa.

Hayes-Campbell, J., 327 Washington, St., Newport, Ky.

Hollick, Herbert, Easton, Pa.

Lewis, Gerald, Box 70, South Bethlehem, Pa.

Love, E. G., Ph.D., 80 East 50th St., N. Y. City.

Ludlow, Gabriel, Sharpsville, Pa.

Mallory, J. Halsey, 361 Monroe St., Brooklyn, N. Y.

Semans, Wm. O., Delaware, Ohio.

Shepherd, Frank I., Kyle, Ohio.

Way, A. B., New Brunswick, N. J.

Wentworth, Walter V., Ticonderoga, N. Y.

Williams, Herbert M., B.S., 124 St. James Place, Brooklyn, N. Y.

ASSOCIATES ELECTED NOVEMBER 2, 1895.

Church, Herbert Kenneth, 112 Martien Hall, Lafayette College, Easton, Pa.  
Hopkins, N. Monroe, 1730 I St., N. W., Washington, D. C.  
Louder, J. Willis, South Easton, Pa.  
Parker, W. F., New Brunswick, N. J.  
Sigman, Alfred S., Easton, Pa.  
Thatcher, Charles J., Easton, Pa.

CHANGES OF ADDRESS.

Behr, Arno, 2266 Second St., San Diego, Cal.  
Bolton, H. Carrington, Cosmos Club, Washington, D. C.  
Dains, F. B., 2421 Dearborn St., Chicago, Ill.  
Ford, Allen P., care of Crane Co., 12th and Canal Sts., Chicago, Ill.  
Forrest, Chas. N., Room 462, Central Power Sta., 14th and Penna. Ave., Washington, D. C.  
Guild, Frank N., Wesleyan Univ., Middletown, Conn.  
Harrison, Herbert E., Box 15, Trenton, Mich.  
Herrick, Wm. Hale, 207 Greenwich St., New York City.  
Hodge, H. B., 1300 Pennsylvania Ave., Washington, D. C.  
Mallory, J. Halsey, 539A Green Ave., Brooklyn, N. Y.  
Tucker, Francis T., 1720 M St., Lincoln, Neb.

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MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

A meeting of the Chicago Section of the American Chemical Society was held October 15.

A Note on the precipitation of zinc in acid solution was presented by Prof. J. B. Nagelvoort.

Dr. J. H. Long gave the results of some experiments on the precipitation of antimony cinnabar from solutions of tartar emetic by means of sodium thiosulphate.

Mr. C. L. Kennicott read some correspondence between Alfred Allen and Mr. Bannister, of Somerset House, Eng.

NEW YORK SECTION.

The October meeting of the New York Section was held in the University Building, Prof. P. T. Austen in the chair.

Prof. Austen was re-elected Presiding Officer for the ensuing year. Dr. Durand Woodman was elected Secretary and Treas-

surer. Profs. A. H. Sabin, A. C. Hale and A. R. Leeds were elected as Executive Committee. Messrs. McKenna and Hale were elected to act with the chairman as delegates to the Council of the Scientific Alliance. Prof. Hale reported for the delegates to this Council for 1894-95. On motion, his report was accepted.

The chair appointed a committee of two to act with the New York Section of the Society of Chemical Industry in giving a complimentary dinner to Messrs. Tyrer and Mond.

The chairman also appointed a committee to draw up suitable resolutions upon the death of Pasteur, the same to be signed by the Chairman and Secretary and forwarded to the French Chemical Society. Messrs. Squibb and Loeb were appointed.

A paper on "Progress of Chemical Work in the Agricultural Experiment Station," was read by E. B. Voorhees; "On the Development of Colors on Vegetable Fibers," by Dr. Baker; "A Laboratory Note Book," "Cold Production of Oxygen," "A Specimen Bottle," and "The Commercial Production of Haematein," by Prof. P. T. Austen; "Quantitative Volumetric Determination of Orcinol," by H. S. Neiman.

The meeting of November 8th was held in the hall of the Mott Memorial Library at 64 Madison Ave., New York, Prof. P. T. Austen in the chair.

The minutes of the previous meeting were read and approved.

The Secretary reported that the letter authorized to be prepared in regard to the death of Louis Pasteur, had been received from the Committee, and duly forwarded to the French Chemical Society.

Prof. W. P. Mason's paper on "The Chemical vs. the Biological Examination of Water" was read by Prof. McMurtrie, in the absence of the author.

In the discussion which followed, the opinion was general, that to arrive at a sound conclusion, it is necessary to make both examinations, and in addition, the history of a water should be known as accurately as possible.

Prof. McMurtrie stated that in examining a large number of wells in the State of Illinois, he had found no cases of typhoid fever from the use of well waters in which the nitrites, free and albuminoid ammonia were all low.

These determinations, in conjunction with careful investigation of the history of a water he had found a pretty safe guide to an opinion.

Dr. Horne described an interesting case of large increase of nitrites in mixing three water supplies, the nitrites being low in each of the waters tested separately. Prof. Speyers suggested that the presence of hydrogen sulphide, or other reducing agent in one of the waters, acting on nitrates in the others might account for this phenomenon.

A paper "On the Heat of Solution of Certain Carbon Compounds" was read by Prof. C. L. Speyers.

Dr. Austen read a "Note on Runge's 'Bildungstrieb' of Substances" and exhibited a copy of this old and rare work.

Mr. Cutts read a paper by T. S. Gladding, "On the Gravimetric Method of Determining Phosphoric Acid by the Phosphomolybdate Method."

"Specimens showing the Effects of Gun-Cotton Explosions" were exhibited by Mr. W. H. Burleigh.

The meeting was then adjourned to the second Friday in December.

#### WASHINGTON SECTION.

The Washington Section of the American Chemical Society held a meeting on May 9th, President Munroe in the chair. Forty members were present. Marion Dasett and S. C. Miller were elected to membership.

The first paper was read by Dr. E. A. de Schweinitz on a new Meteorite from Forsyth County, N. C. The second was by Dr. Peter Fireman, on "Hydrogen Fluoride Poisoning." Discussion by Messrs. Munroe, Brown and Chatard. Prof. Munroe thought that cases like that of Dr. Fireman should be brought together in order that similar accidents could be guarded against and remedies provided. Mr. Brown referred to a work in French upon such accidents; Dr. Chatard referred to similar experiences of his own with hydrogen fluoride. The next paper was by Dr. W. H. Seaman, on "Progress in the Manufacture of Artificial Musk." He stated that the artificial product is a commercial article, and traced its history from the time it was first prepared in 1759 by Markgrof down to the present time, refer-

ring to the different patents issued for artificial musk. The one most known is the Musk Bauer. None of the compounds are in any specific sense artificial musk. A large number of nitro bodies possess valuable odors and synthetic chemistry is trying to supplant the natural bodies. In the manufacture of soap the artificial substance is extensively used.

The subject for discussion for the evening was "The Chemical Action of Micro-organisms." Dr. de Schweinitz opened the discussion by referring to the difficulty of treating the subject in a limited time, and spoke of the vast number of micro-organisms by which changes in the mineral, animal and vegetable kingdoms are produced and of the very few that up to the present time had been isolated and studied. He then described the substances resulting from the fermentations of glucose alcohol and the part played by the different germs in these fermentations and of their selective action. Different germs acting upon the *same* substance produce different results, and the same germ acting upon *different* substances produce the same results. The products of pathological bacteria are complex and difficult to isolate, but it is to them that the fatal effects of diseases are to be attributed. The poisonous products belong for the most part to the toxins that have been isolated from cultures of the different bacilli: tetanus, cholera, diphtheria, tuberculosis and glanders. The albuminoids for the most part are rich in phosphorus, and seem to be more nearly like the nucleins. The quantity produced is so extremely small that it is difficult to make absolute identifications, but they are extremely virulent even in most minute quantities. The pathological power of germs is often decreased or diminished; they become attenuated and are no longer fatal in their effects, either because they do not find the soil adapted to their multiplication or because the amount of active poison secreted is too small. The germs are interesting also on account of the composition of their own bodies; this is constant, but different for different forms. The proximate constituents are varied. For instance, the percentage of fat is very different in the different bacilli. Some of the germs produce cellulose and others do not. The different effects produced by them must result from the internal structure of the molecules.

Surgeon General Sternberg, who was present as a guest, gave a brief outline of some of the products of pathological bacteria, referring to the work of Brieger, Pfeiffer, Kitasato and others. The toxins may be acids or bases unstable, or united with the colloid bodies. "Toxalbumens" may be continued as the term to apply to them.

Prof. Wiley said that micro-organisms were at work in the interest of the farmer long before there were any medical schools. He referred to the intimate relations that existed between certain minute organisms and the chemical reactions which take place in the soil.

Prof. George P. Merrill, who was present as a guest, was called upon and said that he was not quite so enthusiastic as Dr. Wiley upon the part micro-organisms played as rock destroyers. They have been found in rocks that are highly decomposed, but he thought it had not been proved that they caused the decomposition. He looked at the subject from a conservative standpoint, partly from the fact that it is one that few geologists have investigated. In the District of Columbia he thought mechanical agencies were more potent than chemical action as rock destroyers. Rocks that disintegrated to the depth of fifty feet lost three per cent. or less of their original constituents. The disintegration goes to the depth of 200 feet. He thought the action of bacilli has been overestimated.

The Society at 10 P. M. adjourned until November.

#### CINCINNATI SECTION.

A meeting of the Cincinnati Section was held on November 15, 1895, Dr. Alfred Springer presiding.

In an interesting talk on "The Glycerol Industry," Mr. Joseph Feemster described the various processes that have been used in the manufacture of glycerol and exhibited samples representing different stages of the process, and the several grades of glycerol now on the market.

In a paper on "The Recent Progress in Cellular Chemistry," Dr. S. P. Kramer gave a resumé of the latest advances in micro-chemical work.

Mr. F. I. Shepherd, of this city, and J. Hayes-Campbell, of Newport, Ky., were elected members of the Section.











